



Investigating the Ability of Plastic Current Collectors to Isolate Internal Shorts



With the European Synchrotron Radiation Facility

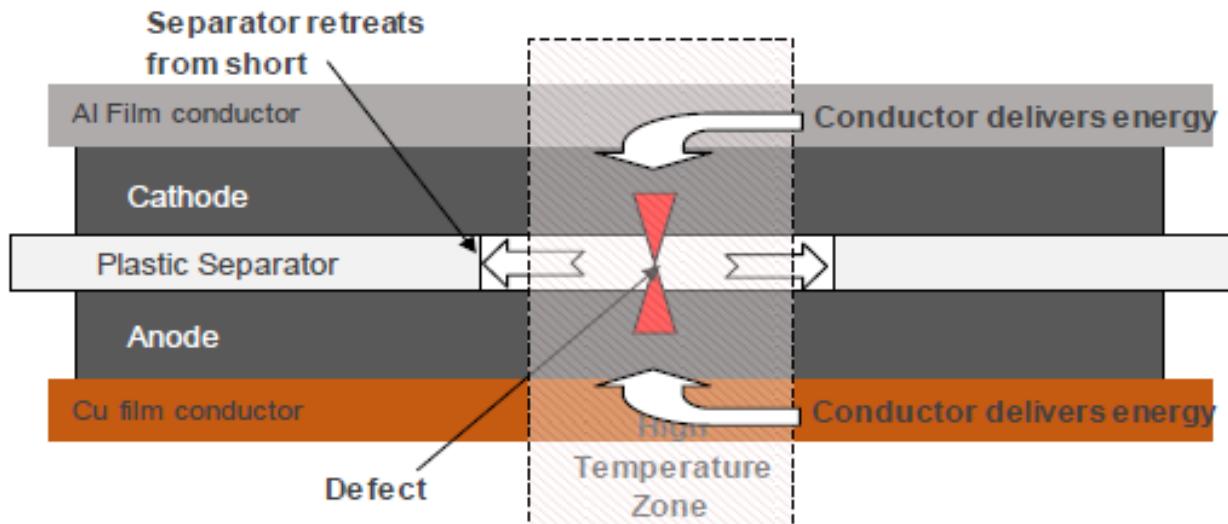
Eric Darcy/NASA-JSC
International Battery Seminar
Orlando, FL
21 Mar 2023

Agenda

- Motivation
 - Determine how these plastic current collectors (PCC) work
 - Obviate battery PPR design burden
- Team Effort
- Cell Designs
 - 18650
 - 21700
 - 10Ah pouch
- Test Plans
- Test and Examination Results
- Forward Work and Summary

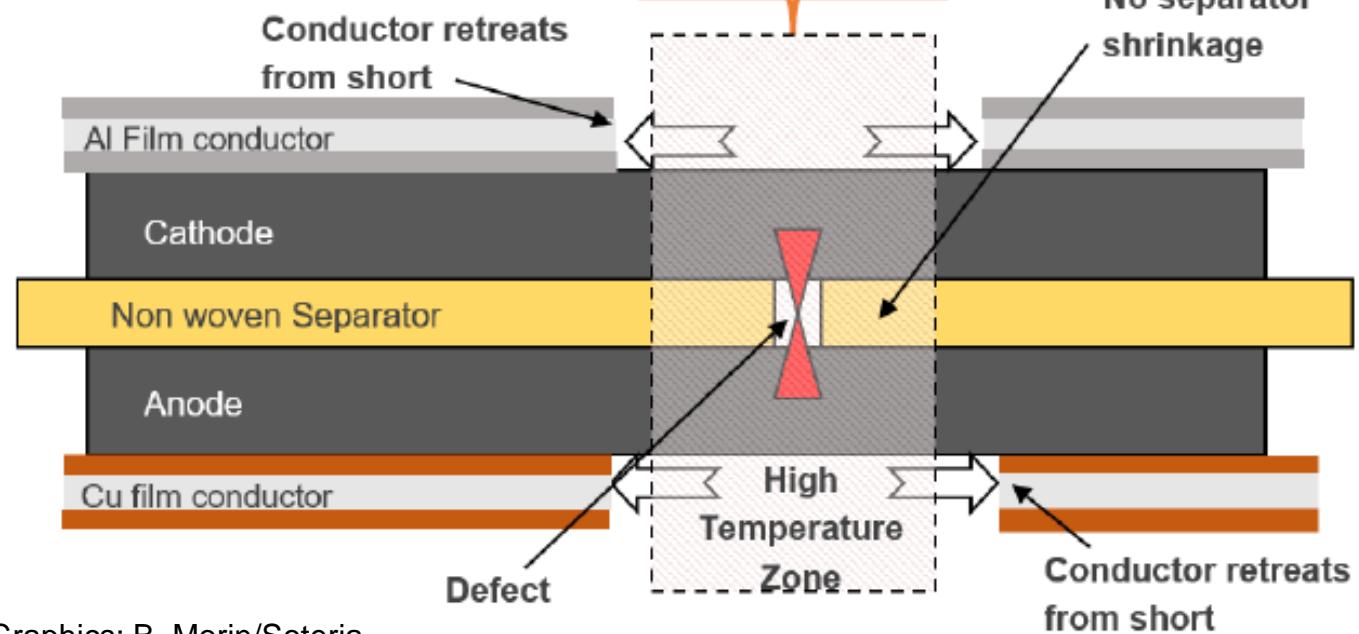
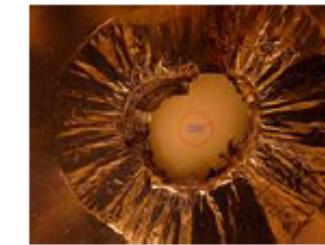


Theory of Metallized Plastic Current Collectors



- Internal short defect is fed rapidly through solid metal (Al, Cu) film current collectors
- Polymer separator thermally breakdowns and shrinks away creating higher internal short risk between anode and cathode

- Plastic substrate of current collector **thermally** breaks down and isolates the electrochemically active materials from the defect within milliseconds



Team Effort



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John Darst



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Dr. Donal Finegan

NREL



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Alexander Rack

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- Donal Finegan/NREL, Golden, CO, USA
- Martin Pham, Charlie Kirchner-Burles, Mark Buckwell, Hamish Reid, Matilda Fransson, and Paul Shearing/UCL, London, UK
- Alexander Rack and Ludovic Broche/ESRF, Grenoble, France
- Joe Turner and Ed Buiel/Coulometrics, Chattanooga, TN, USA
- Brian Morin & Carl Hu/SoteriaBIG, Greenville, SC, USA
- France Rochette/Dupont, USA

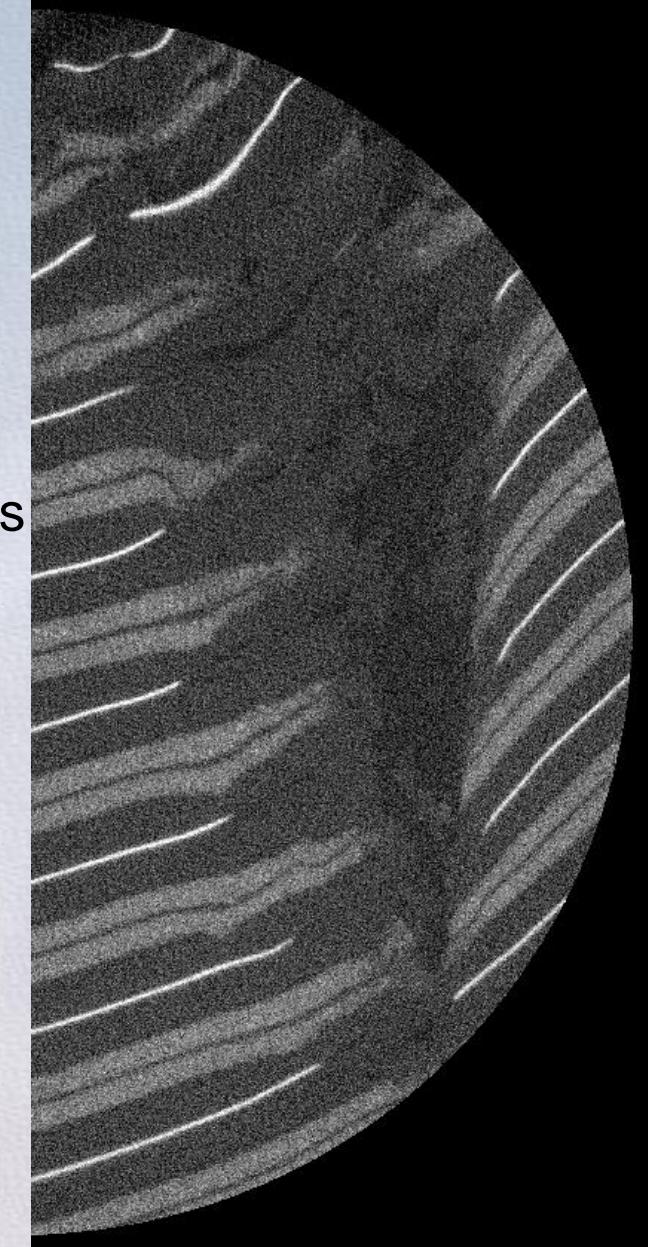
Acknowledgements

Thanks for the sponsors of our cell strategic reserve for funding this effort

- Orion, CCP, HLS, and NAVSEA

Findings from 2018-2019 Plastic CC Cell Builds & Tests

- Mixed tolerance to the nail in 2.1Ah 18650 cells¹
 - Post test CT imaging again shows the plastic collector vaporizing and isolating the active material from the shorting defect on about 50% of cylindrical cells
 - Overall, of the cells driven into TR, plastic collector films lower the calorimetric output vs metal foil cells
 - Plastic collector cells are harder to drive into TR than metal foil cells
 - TR is less violent than with metal foil cells (thermite rxn?)
 - Collector films show no cycle life impact to date (300 cycles)
- No tolerance to ISC device¹
 - Standard 1kW heating of cell chamber overwhelms cell and drives it into TR
- Microfocus CT images by UCL of surviving cells reveals absence of PCC at and near nail interface²



1. Darcy et al, International Battery Safety Workshop, Beijing, China, Oct 2019

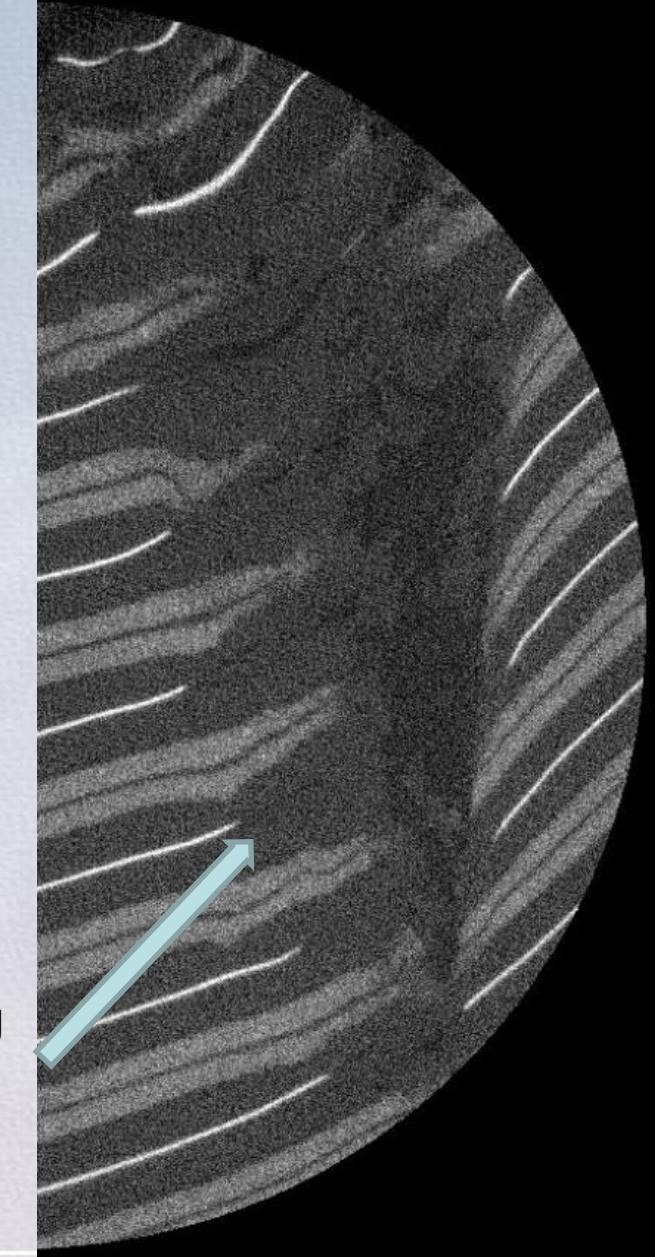
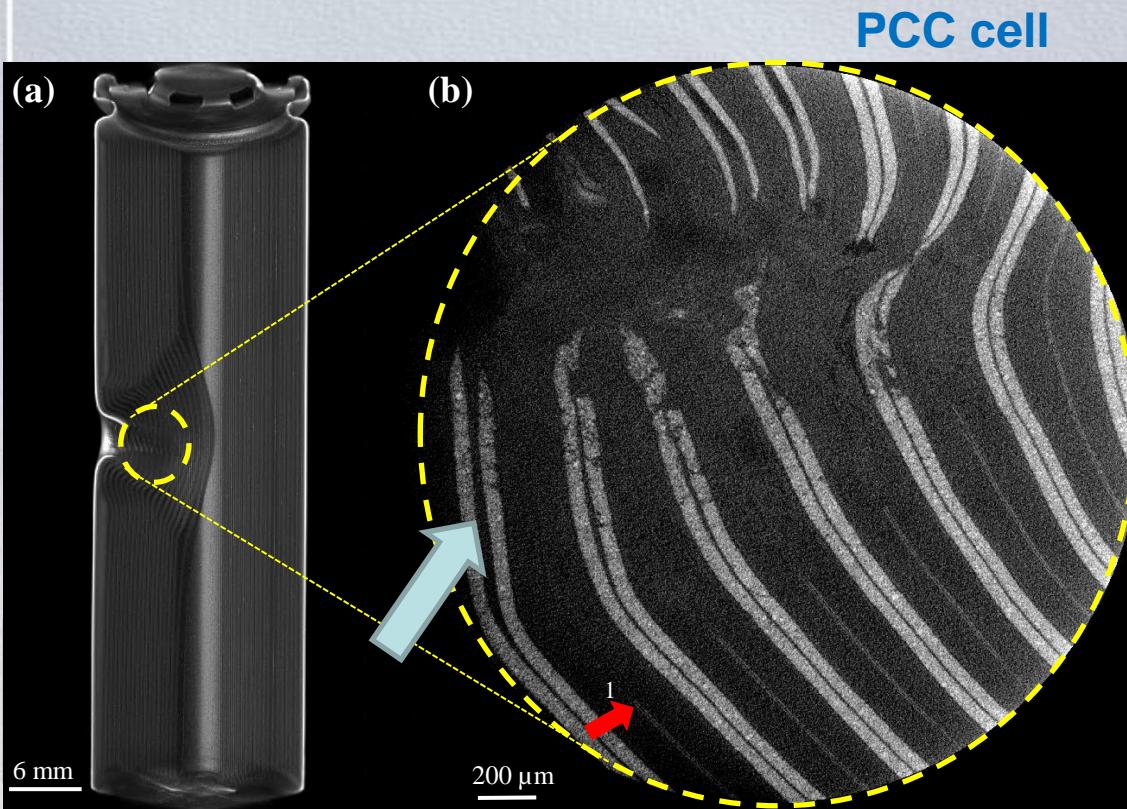
2. Pham et al., Cell Reports Physical Science 2, 100360, Mar 2021

Results: Thermal Effect

Data from 2020

Bright CC is Cu PCC coated with darker graphite
Cathode PCC is gray layer substrate for bright NMC

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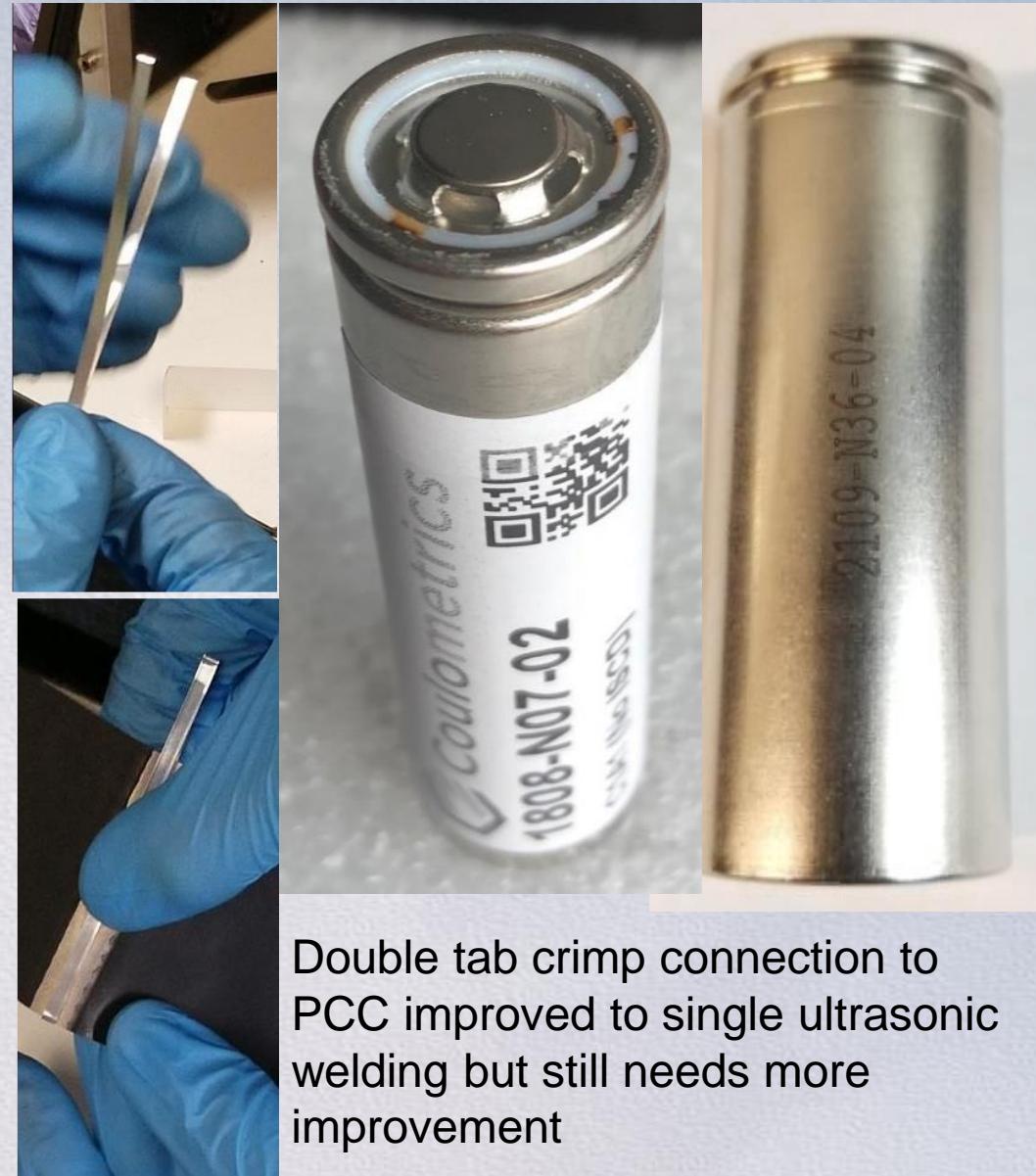


X-ray CT reveal Al and Cu PCCs withdrawn from the nail, thus reducing further short-circuiting. OCV measurement showed 4.07 V; cells retained voltage for over 10 months.

Newest Coulometrics 18650 Cell Builds

Metallized plastic current collectors

- 10 μm polyester films coated with Cu and Al (0.5 to 1.0 micron) from Soteria
 - 2.1Ah Graphite/NMC with Dreamweaver Gold cellulose separator
 - Only cathode PCC replaced (~88 m Ω)
 - Anode & cathode PPC replaced (~280 m Ω)
 - Controls (~21 m Ω)
 - Built in 2020
- 20 μm Nomex films coated with Cu and Al (0.5 to 1.0 micron) from Dupont
 - 2.1Ah Graphite/NMC with polyolefin separator
 - Only cathode PCC replaced (~36 m Ω)
 - Anode & cathode PPC replaced (~88 m Ω)
 - Controls (~20 m Ω)
 - Built in 2021

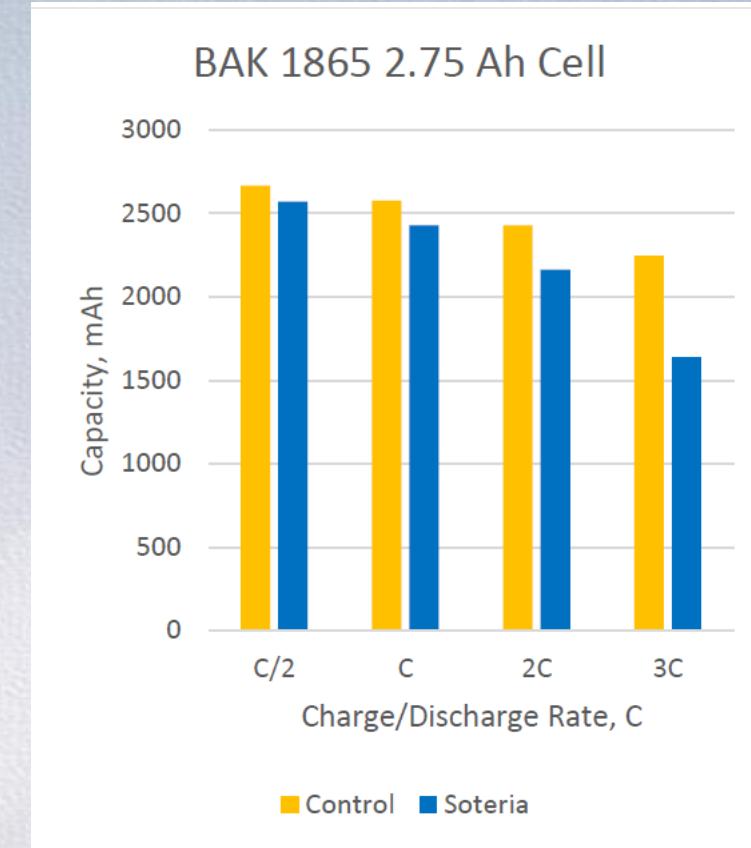


Double tab crimp connection to PCC improved to single ultrasonic welding but still needs more improvement

BAK 18650 Cell Designs

Soteria Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Soteria Al, Standard Cu
Nominal Voltage	3.6V
Capacity	2.75Ah
AC impedance	51 mΩ
Weight	44 g
Energy Density	200 Wh/kg
Voltage Range	2.5V-4.2V

Control Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Standard Foils
Nominal Voltage	3.6V
Capacity	2.75Ah
AC impedance	34 mΩ
Weight	45 g
Energy Density	209 Wh/kg
Voltage Range	2.5V-4.2V

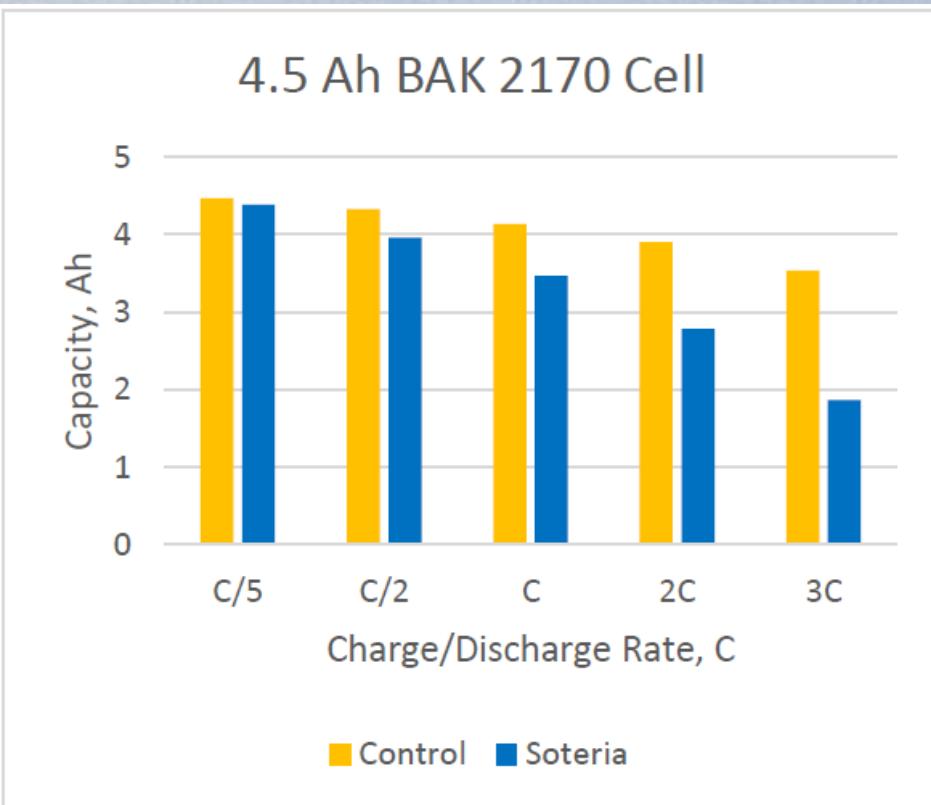


- Soteria polyester PCC only applied to cathode
- Impressive power capability (2C) with Soteria's PCC, not too far behind control cells
- They have found a decent tab to PCC welding schedule

BAK 21700 Cell Designs

Soteria Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Soteria Al, Standard Cu
Nominal Voltage	3.6V
Capacity	4.5Ah
AC impedance	42 mΩ
Weight	66 g
Energy Density	205 Wh/kg
Voltage Range	2.5V-4.2V

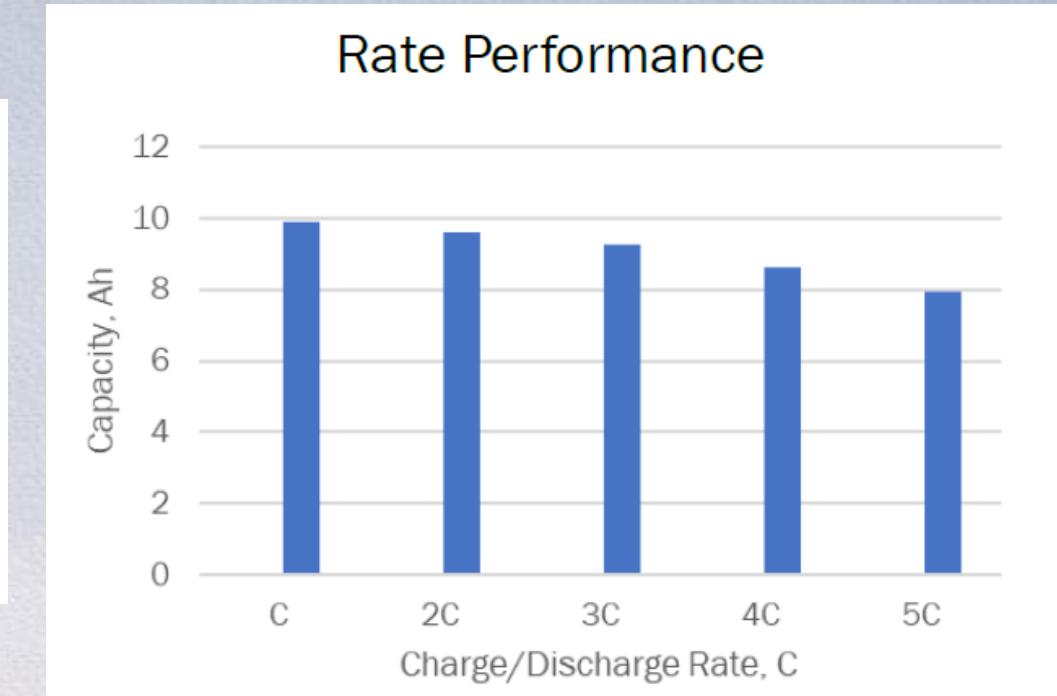
Control Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Standard Foils
Nominal Voltage	3.6V
Capacity	4.5Ah
AC impedance	20 mΩ
Weight	67 g
Energy Density	227 Wh/kg
Voltage Range	2.5V-4.2V



- Soteria polyester PCC only applied to cathode
- Decent power capability (up to 1C) with Soteria's PCC, not too far behind control cells
- They have found workable tab-to-PCC welding schedule

SVolt 10Ah Pouch Cell Design

Cell Specifications	
Manufacturer	SVolt Energy
Separator	Polyethylene w/ ceramic coating
Current Collector	Soteria Al Standard Cu
Cathode Material	NCM 811
Anode Material	Synthetic Graphite
Capacity	10Ah
Voltage Range	3.0-4.2V
Energy Density	240 Wh/kg



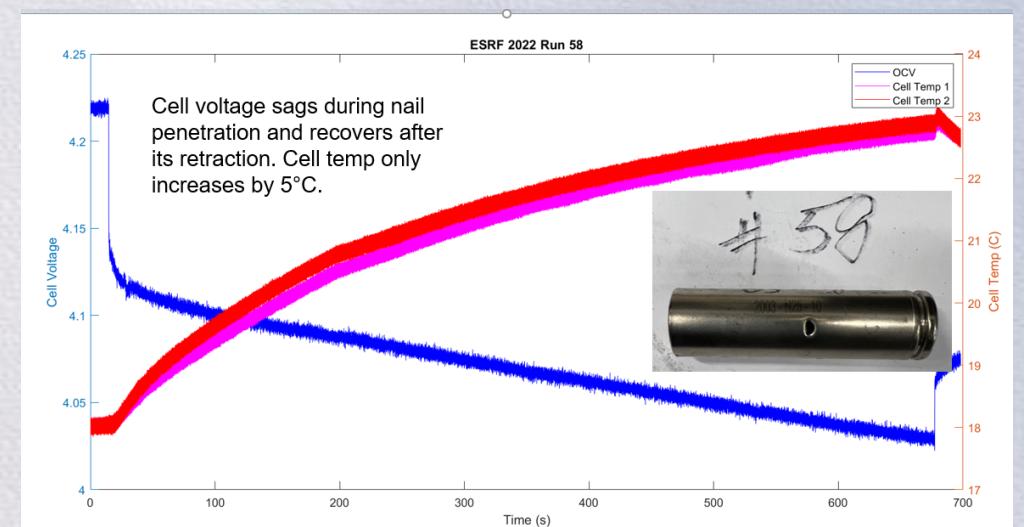
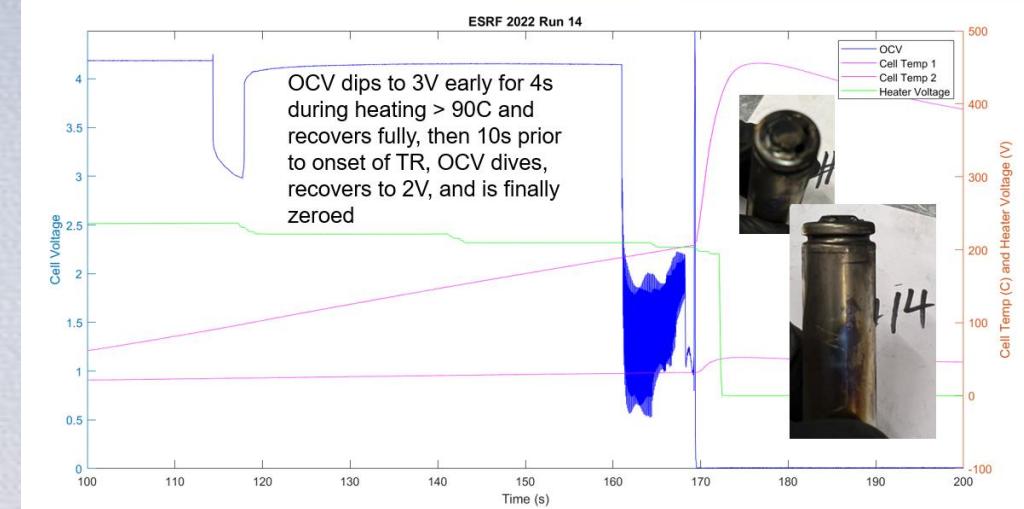
- Soteria polyester PCC only applied to cathode
- Very impressive power capability (up to 5C) with Soteria's PCC
- They have found a great tab-to-PCC welding schedule

2022 Test Series

Feb at ESRF

- Cells
 - 2.1Ah 18650 by Coulometrics
 - Soteria polyester and Dupont Nomex metalized PCC
- Results summary
 - All cells with ISC device driven into TR by overwhelming heat but most showed OCV signs of isolation attempts
 - 100% tolerance to nail with Soteria PCC (3 cells)
 - 33% tolerance to nail with Dupont PCC (3 cells)

Soteria anode & cathode PCC and ISCD driven by heat

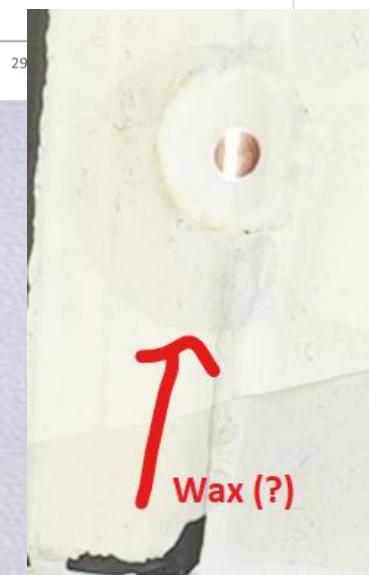
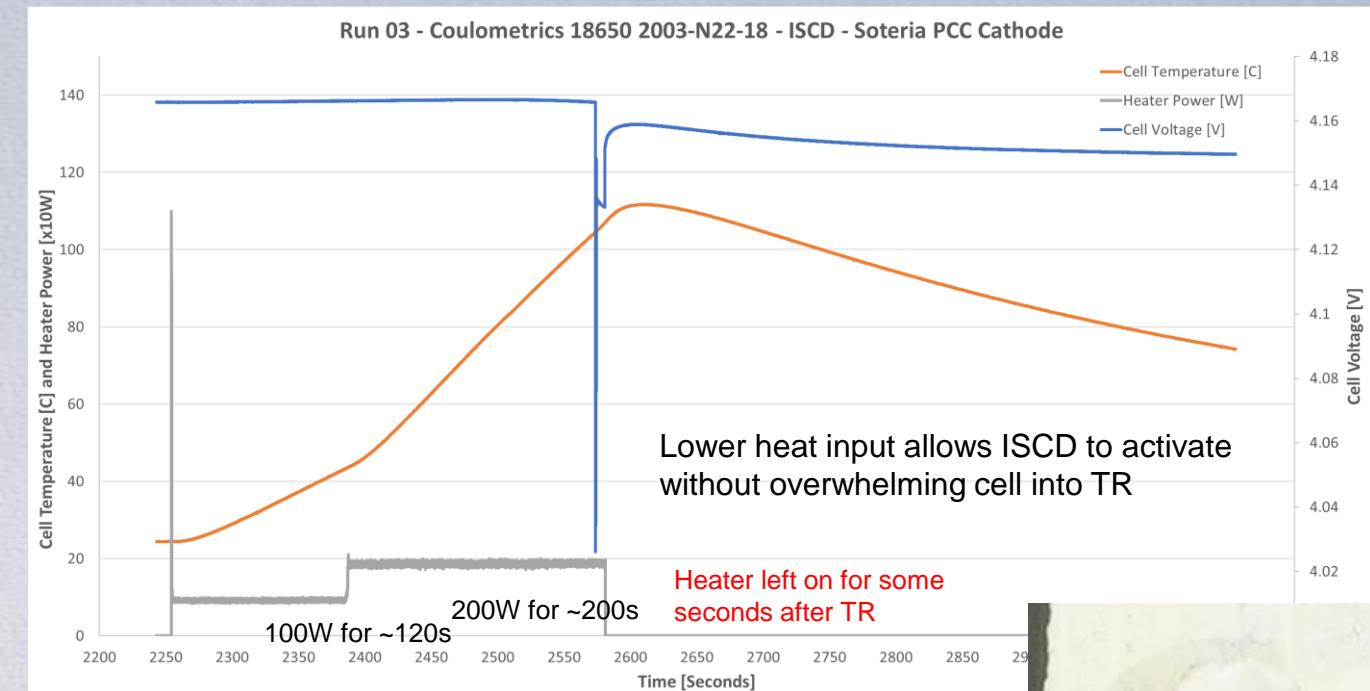


Soteria anode & cathode PCC driven by nail

2022 Test Series (Cont.)

During July at NASA-JSC

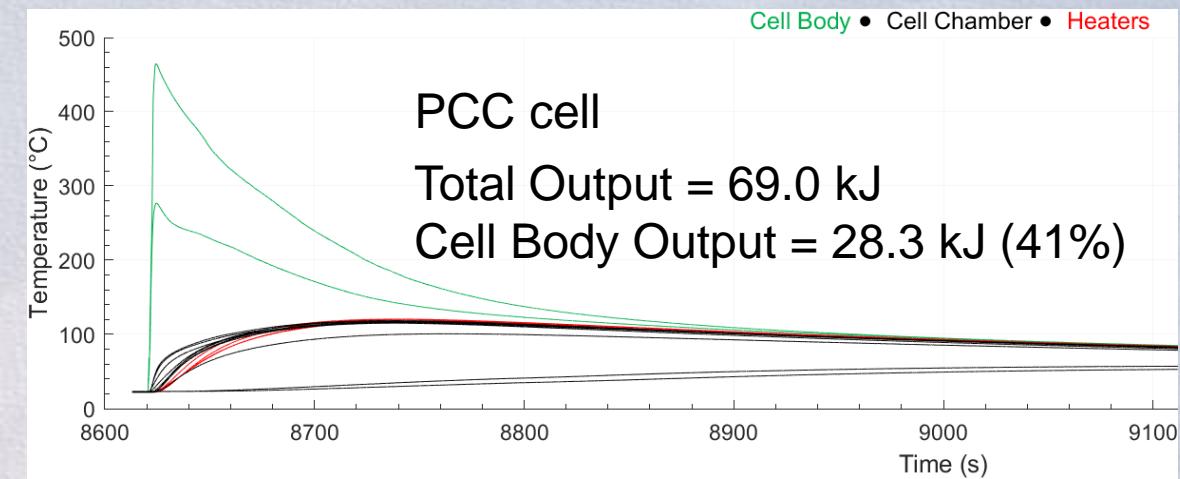
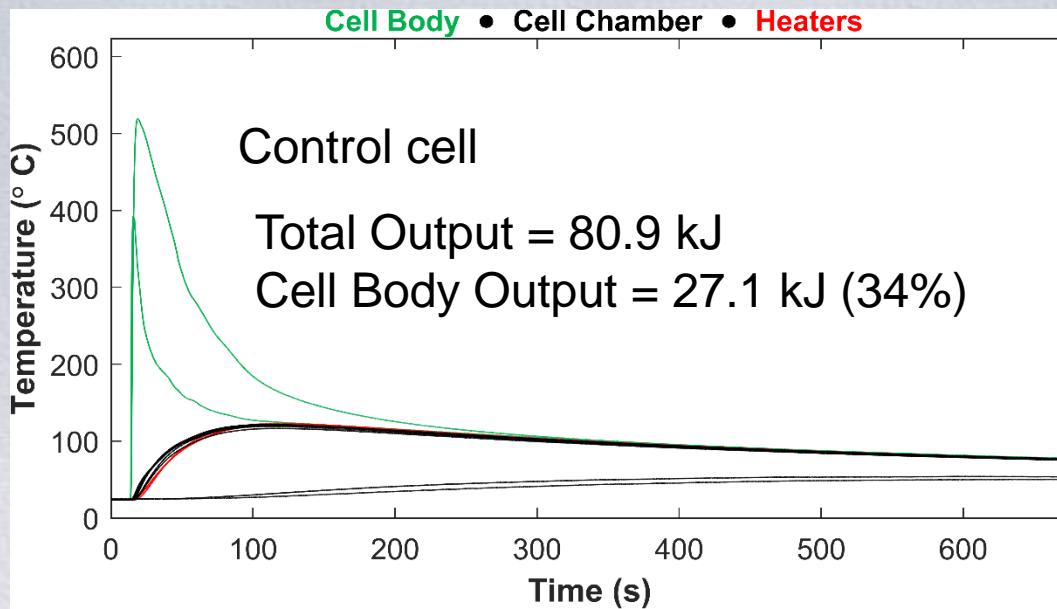
- Cells
 - 18650 (Coulometrics, BAK)
 - 21700 (BAK)
 - Svolt Pouch
- Results summary



PCC Test Runs	Coulometrics		SVolt	BAK with Nail	
	ISCD	Nail		21700	18650
Total	8	7	4	3	3
Successful	6	7	4	2	3
Failure	2	0	0	1	0
Percent Success	75%	100%	100%	66%	100%

BAK 21700 cell TR with PCC films reached 275°C while reaching >500°C with Al/Cu foils

BAK 21700 PCC Failure

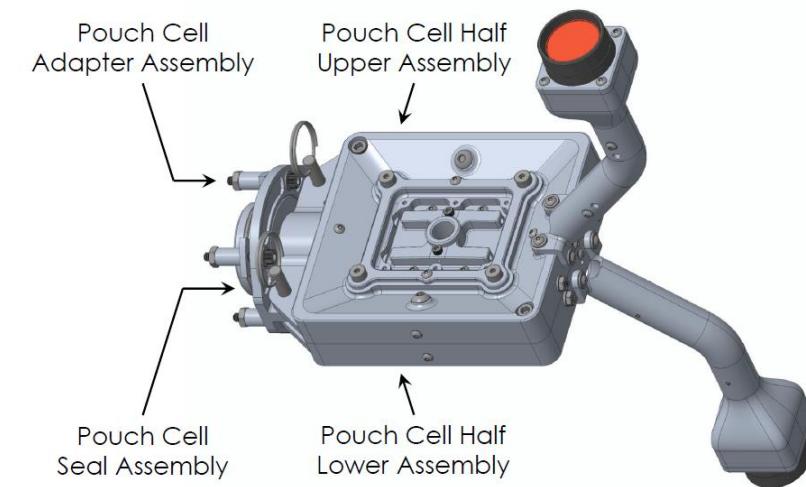


The 1 PCC cell (out of 38) that achieved TR produced 24% less total energy than 4 control cells, but equivalent can wall body energy output than its control cells.

New FTRC Cell Chambers for Pouch Cells

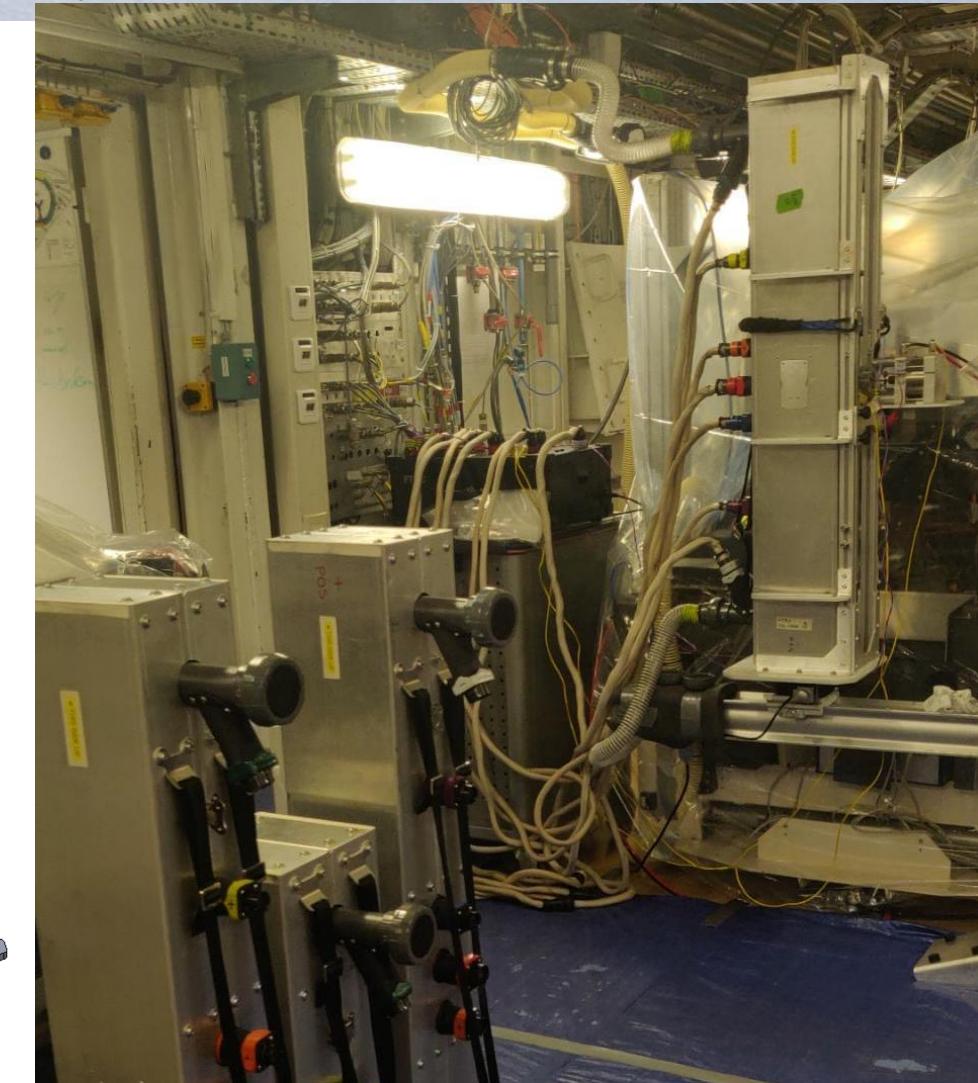
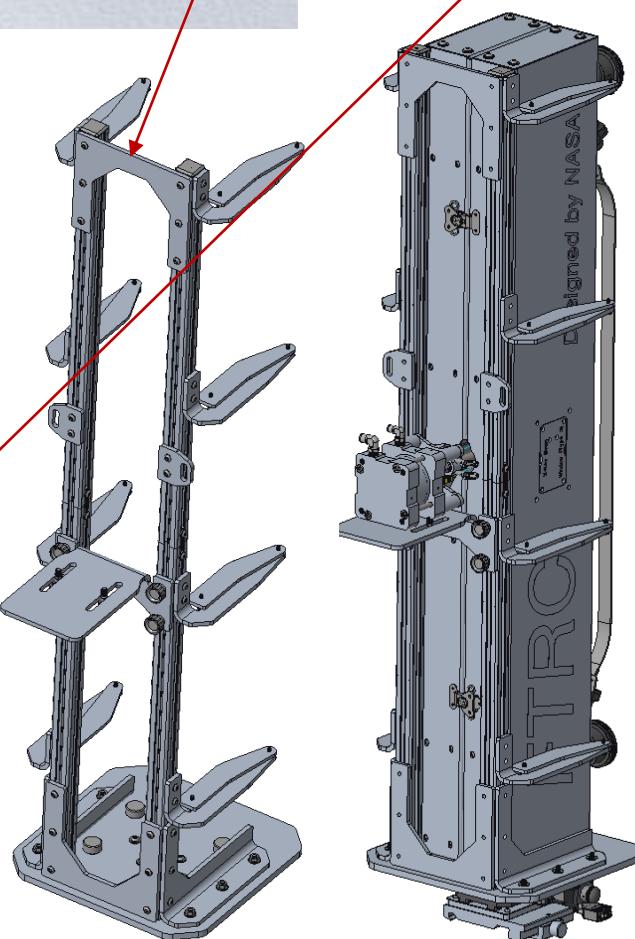
- Clamshell design with all TCs on secured on external surfaces
 - Improves survivability and consistency of measurement
- Only 4 fasteners to secure perimeter O-ring seal and compress the cells
 - Easy installation and quick turnaround
- Chamber adapter enables assembly to plug directly into FTRC bore assembly
 - Held in place with compression seal and shear pins

Pouch Cell Assembly



Improvements for Sep 2022 ESRF

- New insulation cases with Foamglas removed from beam path
- New fine precision rotation stage to align pouch cell electrodes with beam
- New stand to secure case



Coulometrics 2.1Ah Test Matrix (Nail)

- Soteria metalized polyester
 - 4 with cathode PCC (no TRs)
 - 4 with anode & cathode PCCs (no TRs)
 - 3 control cells with metal CCs (all TRs)
- DuPont metalized Nomex
 - 1 with cathode CC (no TR)
 - 1 with anode & cathode PCCs (no TR)
 - 1 control cells with metal CCs (TR)

Tolerance demonstrated with minimal degradation of OCV!!!



CT Images of Coulometrics 18650 with Polyester Anode & Cathode PCCs

Dense material appears bright (cell can, NMC)

Axial view of nail penetration zone



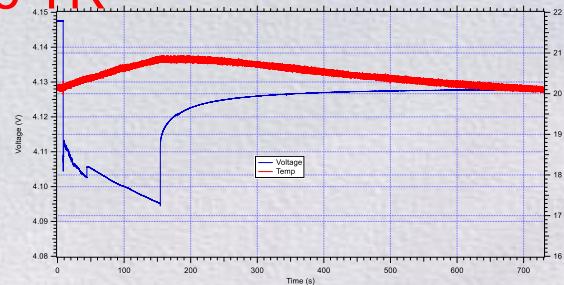
Radial view of nail penetration zone



PCC not present at nail interface, presumably vaporized

BAK 18650 2.75Ah Test Matrix and Results (Nail)

- Soteria metalized polyester (3)
 - PCC only on cathode
 - Cu foil on anode like all other features in control version
 - All 3 cells tolerated nail penetration
 - No fire, sparks, venting, or TR
- Control cells (3)
 - Al and Cu foil CCs
 - All 3 cells went into TR



$$\Delta t_{\max} < 1^\circ\text{C}$$

$$\Delta V_{\max} < 55\text{mV}$$



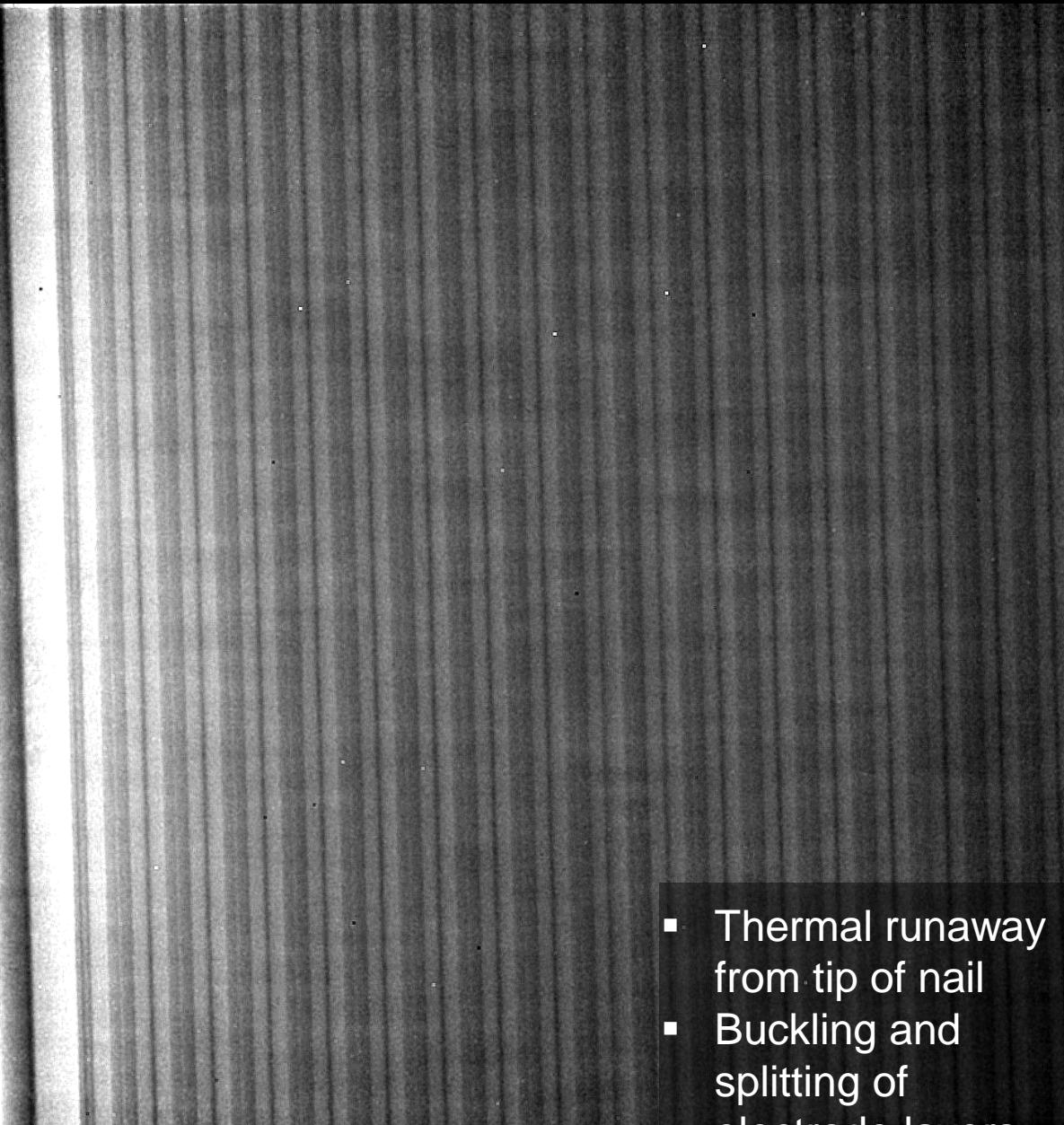
Tolerance demonstrated with near zero degradation of OCV!!!

Radiography at 3000 fps of 18650 cells

Dense material is dark (nail, can, NMC)

Control cell

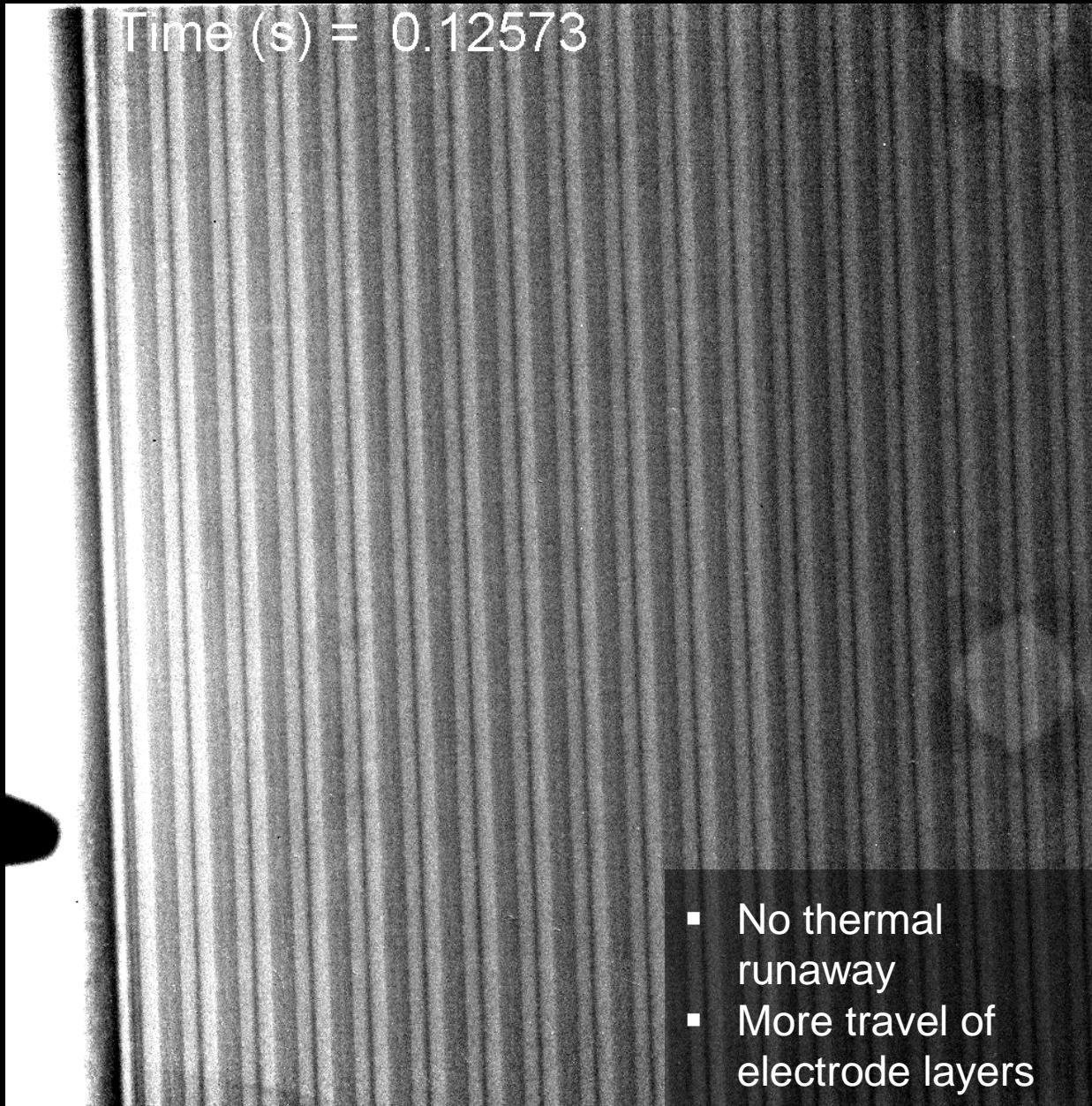
Run 034



- Thermal runaway from tip of nail
- Buckling and splitting of electrode layers

Cell with PCC

Run 031

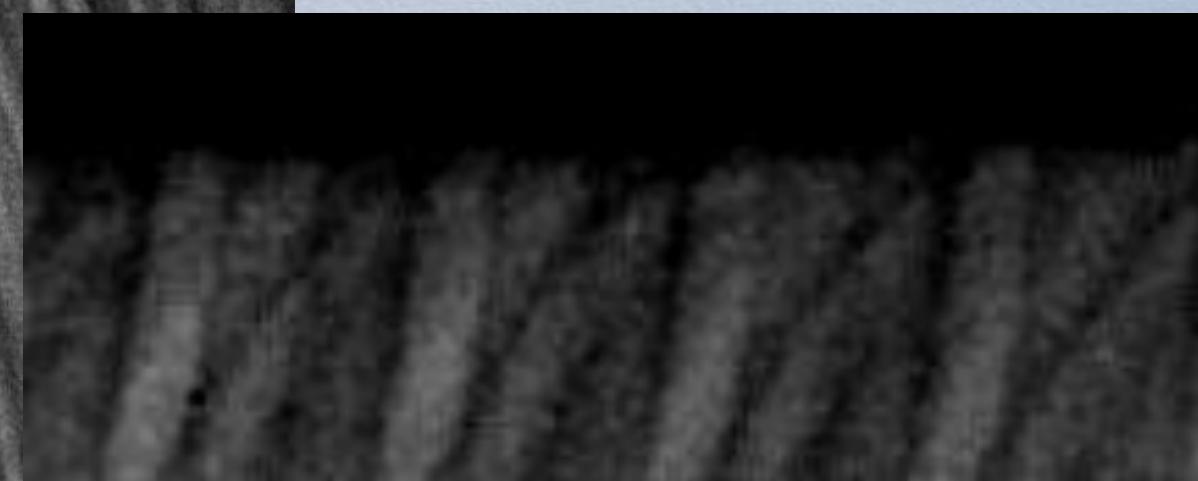
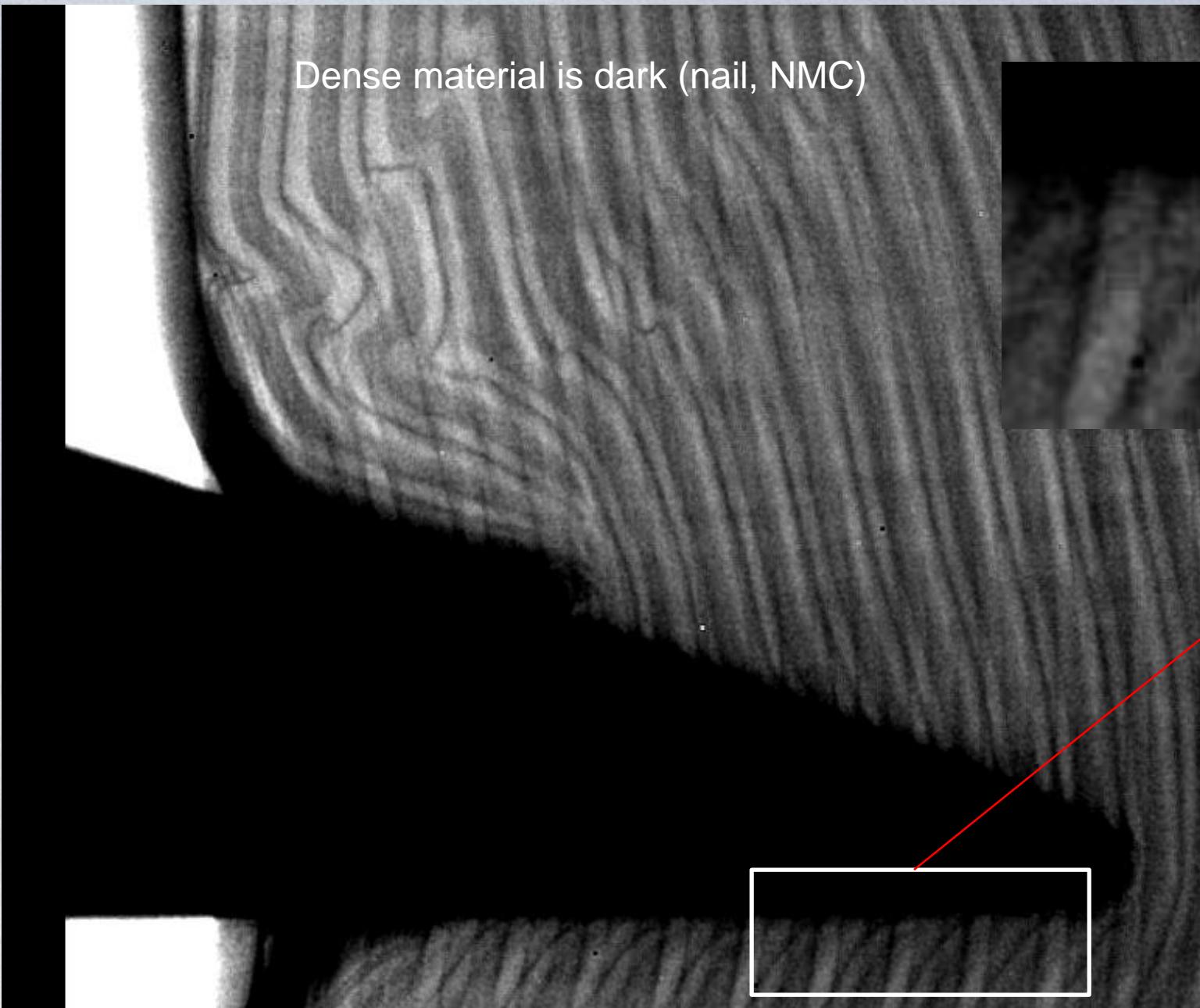


Time (s) = 0.12573

- No thermal runaway
- More travel of electrode layers

Close-up

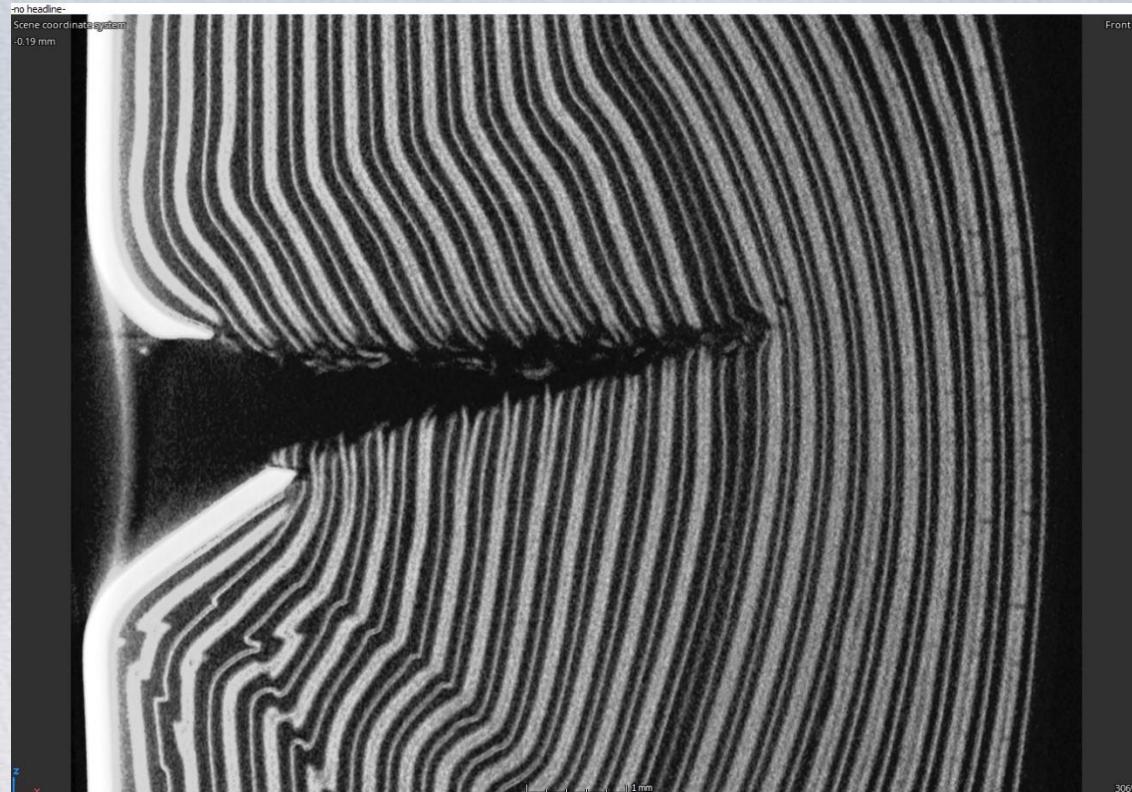
Dense material is dark (nail, NMC)



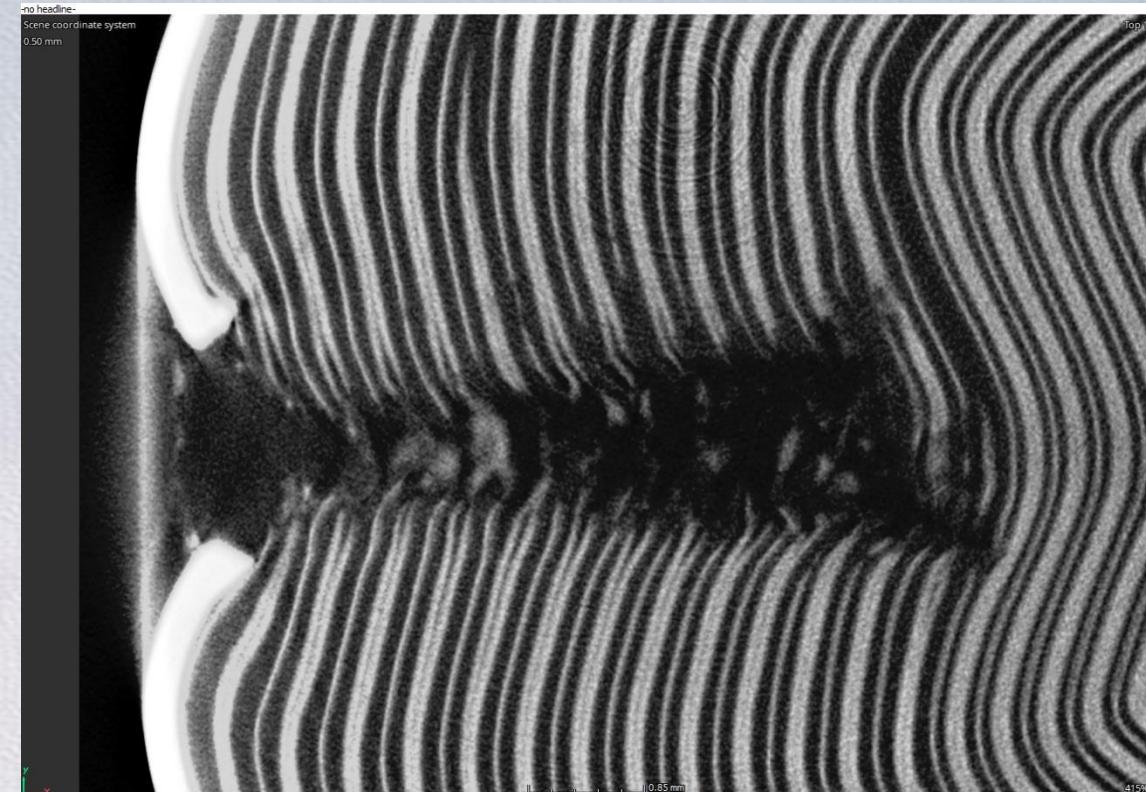
- Cathode material appears to be missing its Al PPC collector at the nail interface

CT Images of BAK 18650 with Cathode PCC

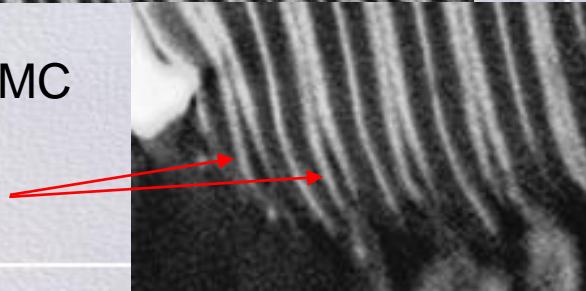
Axial view of nail penetration zone



Radial view of nail penetration zone

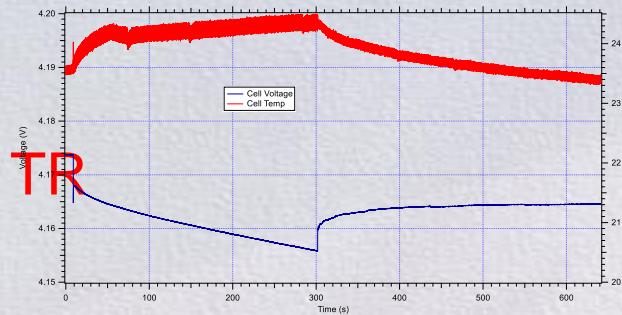


Reversing the image brightness from the video: Bright is most dense material, cell can, NMC
Al coated PCC for cathode is thin gray layer between NMC active material coatings
Axial and radial view show cathode PCC is clearly missing at nail interface (split ends)



BAK 21700 4.5Ah Test Matrix and Results (Nail)

- Soteria metalized polyester (3)
 - PCC only on cathode
 - Cu foil on anode like all other features in control version
 - All 3 cells tolerated nail penetration
 - No fire, sparks, venting, or TR
- Control cells (3)
 - Al and Cu foil CCs
 - All 3 cells went into TR



$$\Delta t_{\max} < 1^\circ\text{C}$$

$$\Delta V_{\max} < 19\text{mV}$$



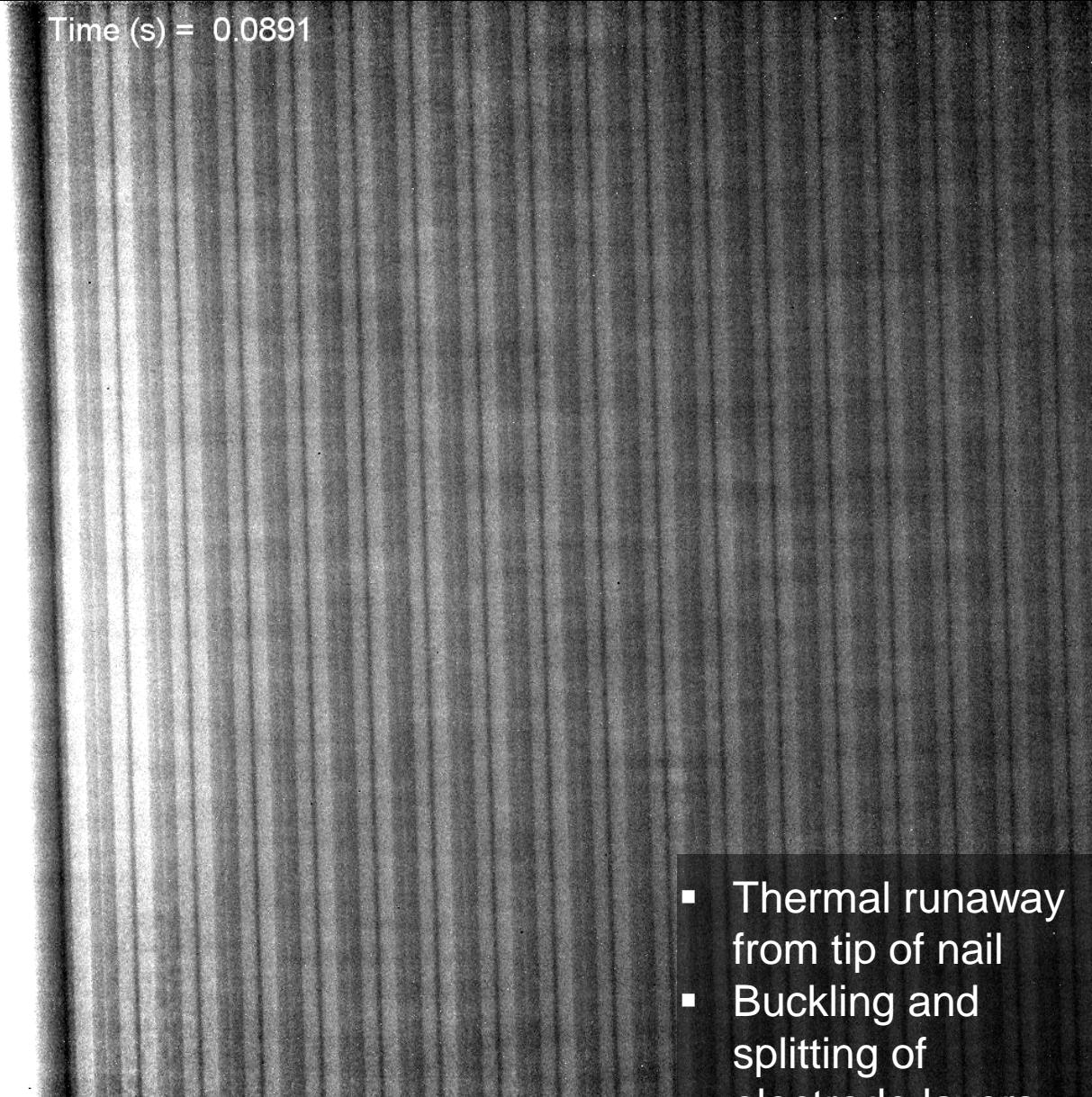
Tolerance demonstrated with near zero degradation of OCV!!!

Radiography at 3000 fps of 21700 cells

Dense material is dark (nail, can, NMC)

Control cell

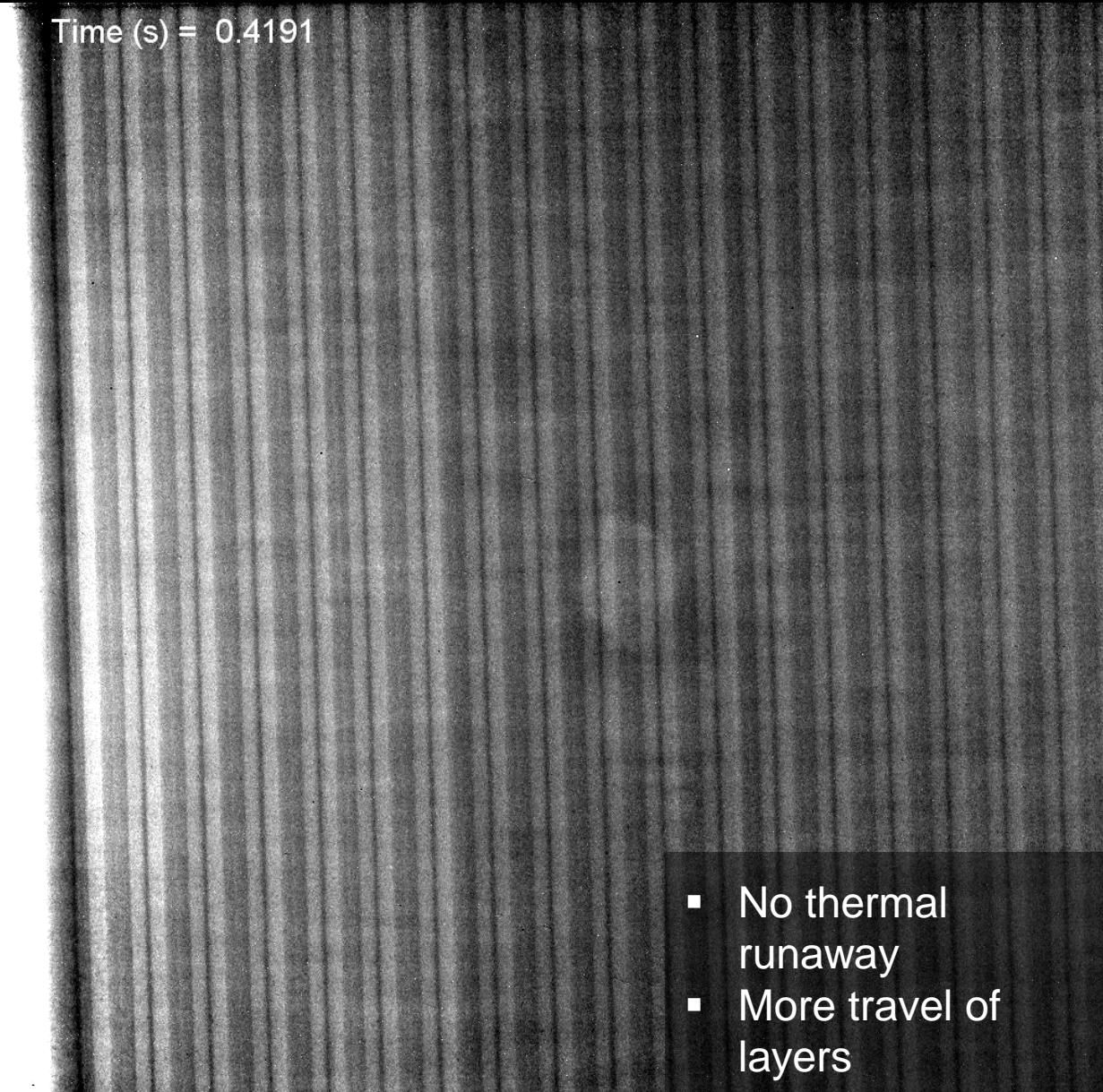
Time (s) = 0.0891



Run 025

Cell with PCC

Time (s) = 0.4191



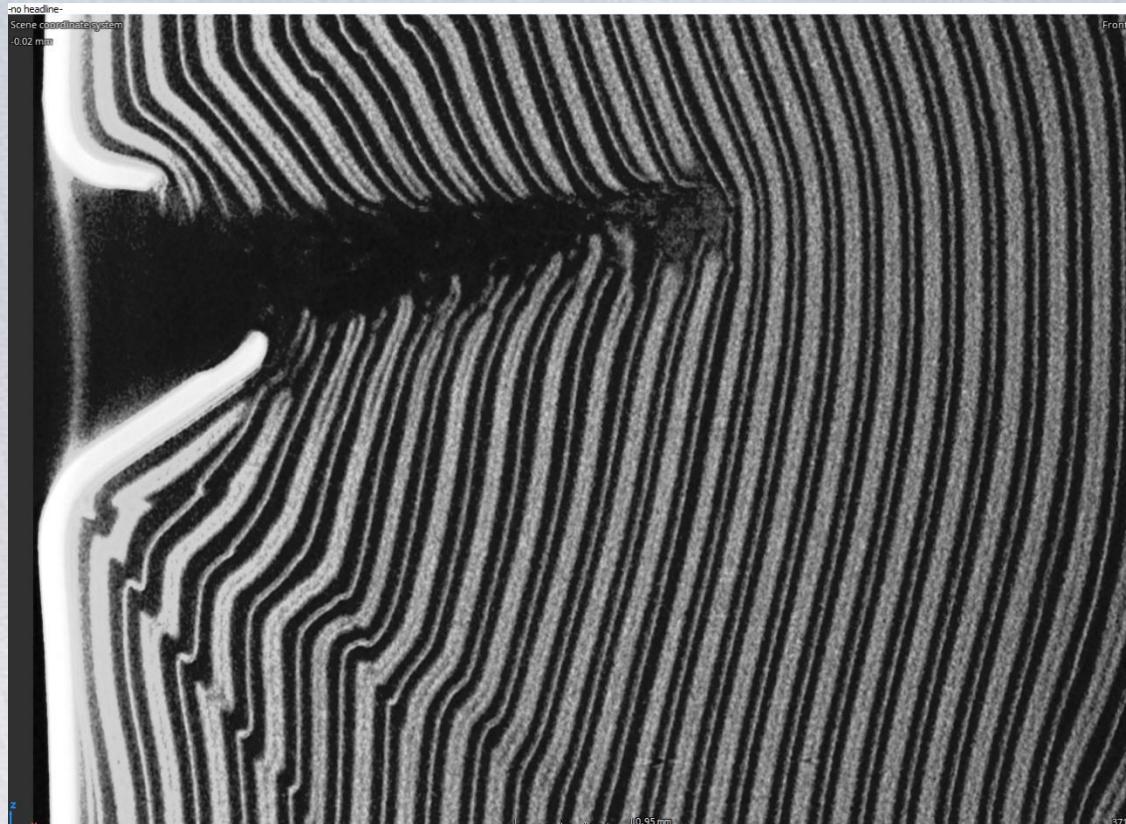
Run 020

- Thermal runaway from tip of nail
- Buckling and splitting of electrodes

- No thermal runaway
- More travel of layers

CT Images of BAK 21700 with Cathode PCC

Axial view of nail penetration zone



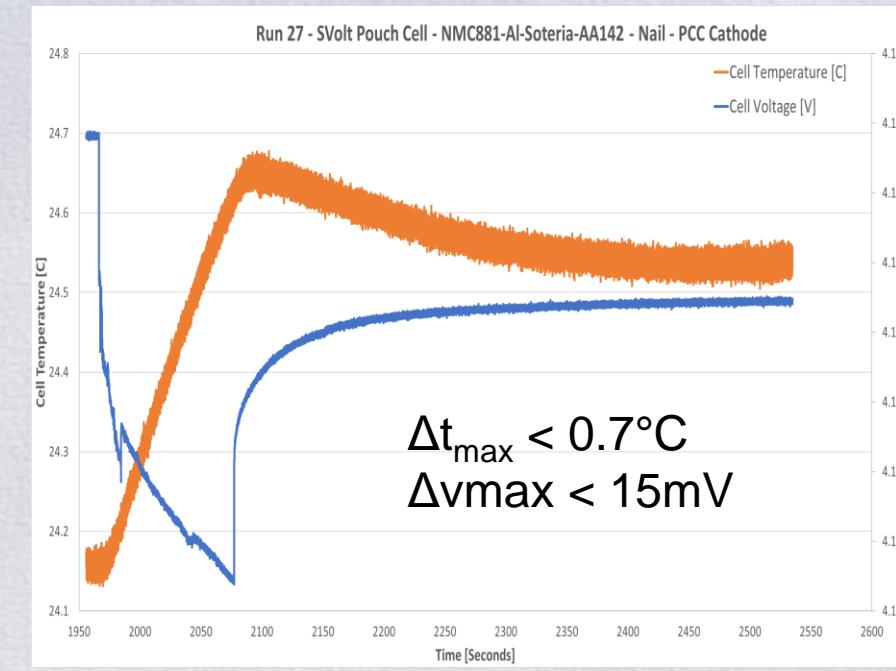
Radial view of nail penetration zone



Reversing the image brightness from the video: Bright is most dense material, cell can, NMC
Al coated PCC for cathode is thin gray layer between NMC active material coatings
Axial view shows cathode PCC is clearly missing at nail interface (split ends)

Svolt 10Ah Test Matrix and Results (Nail)

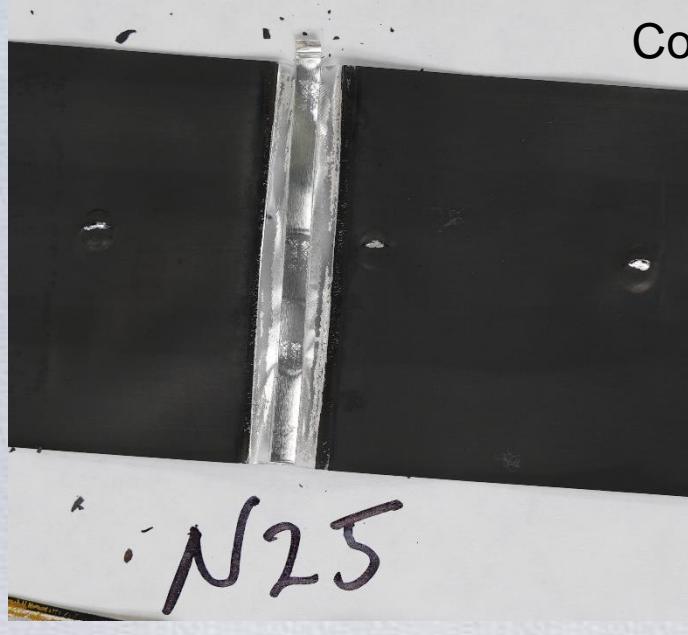
- Soteria metalized polyester (4)
 - PCC only on cathode
 - Cu foil on anode like all other features in control version
 - All 4 cells tolerated nail penetration
 - No fire, sparks, venting, or TR
- Control cells (4)
 - Al and Cu foil CCs
 - All 4 cells went into TR



Only 14mV dip and 0.7°C rise during 2min nail penetration!!!



Coulometrics 18650 Cathode



Coulometrics 18650

Welding Challenges

Coulometrics 18650 Anode



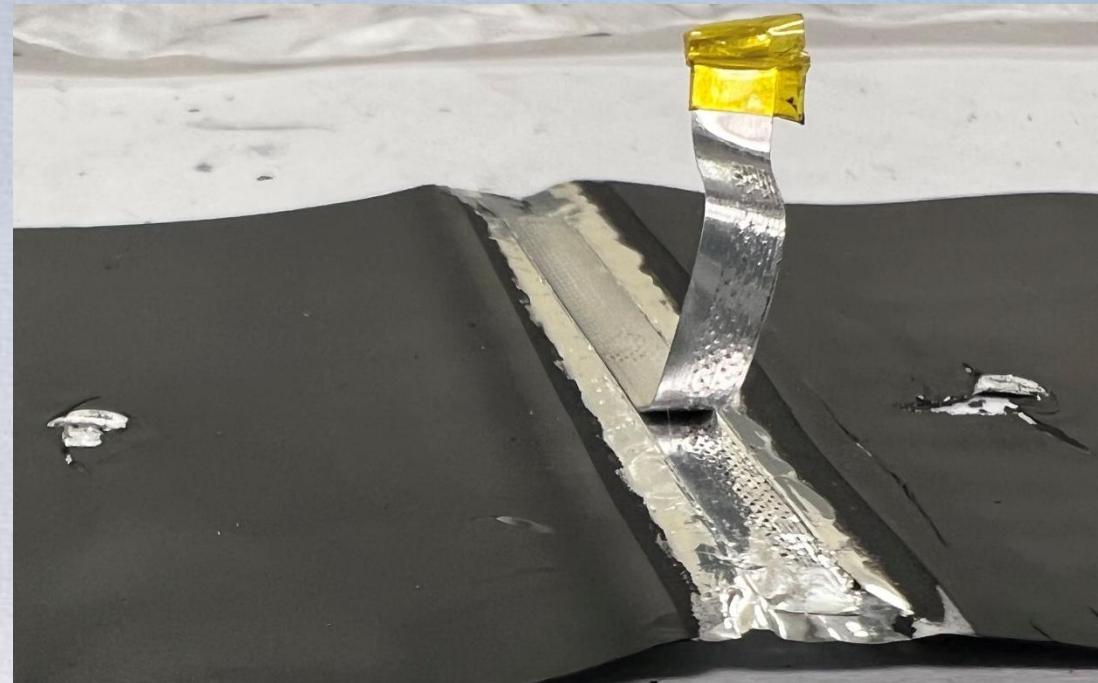
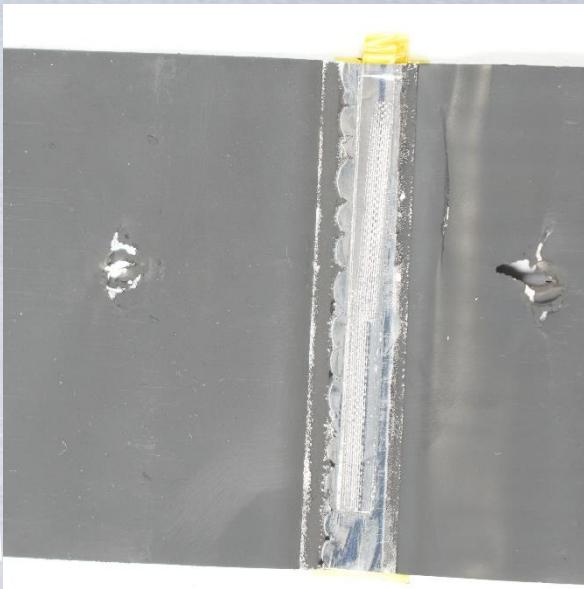
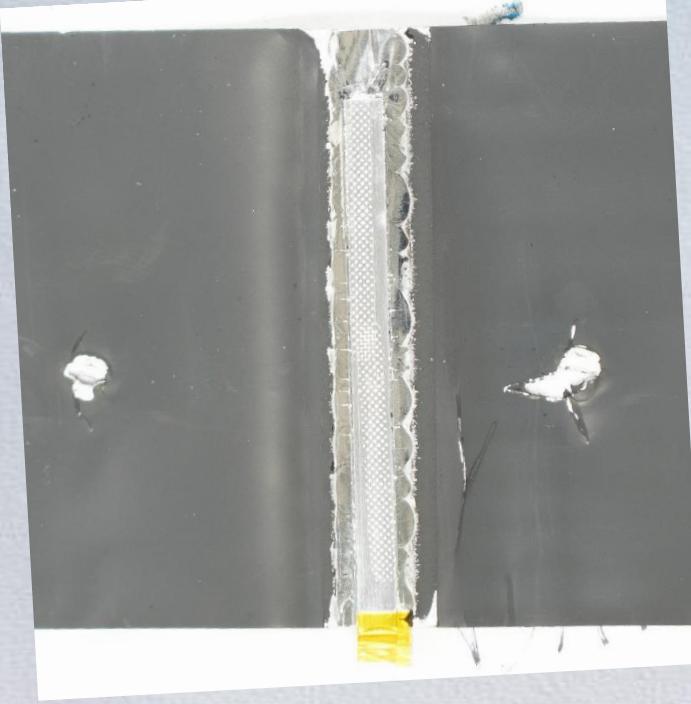
Single tab weld connections to PCC causing >50% increase in ACR vs metal foil cells

BAK 18650 Cathode

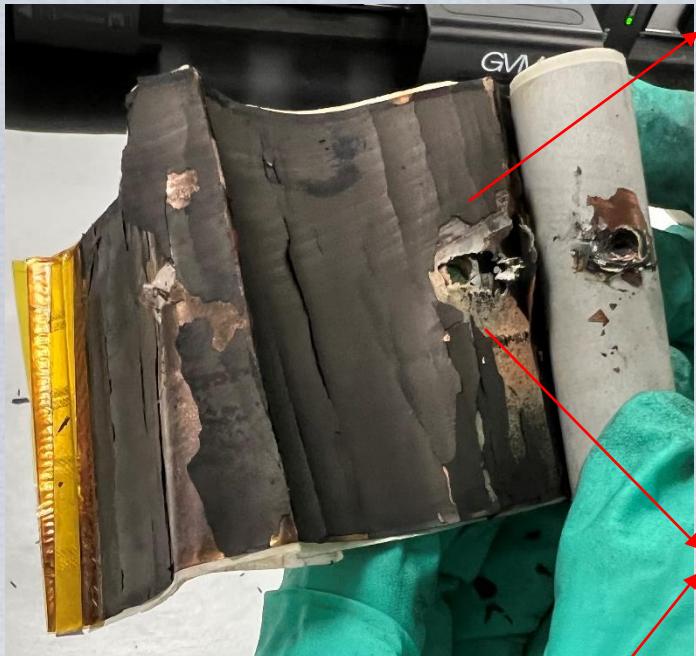


BAK 18650

BAK 21700



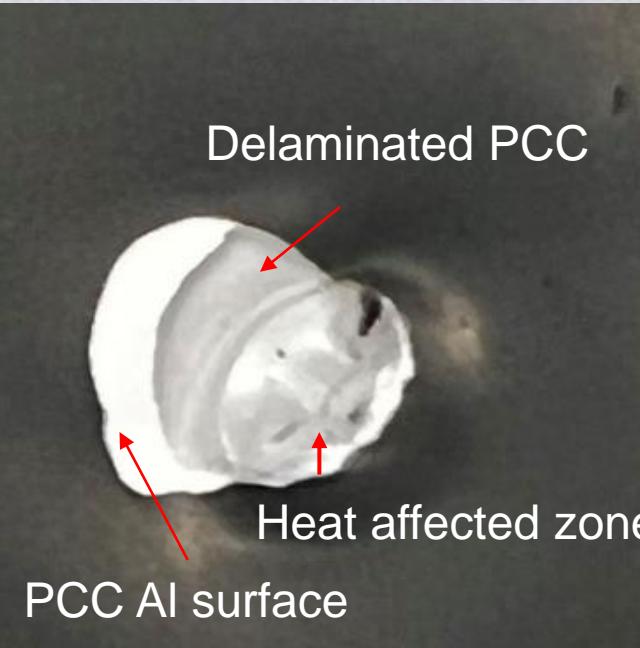
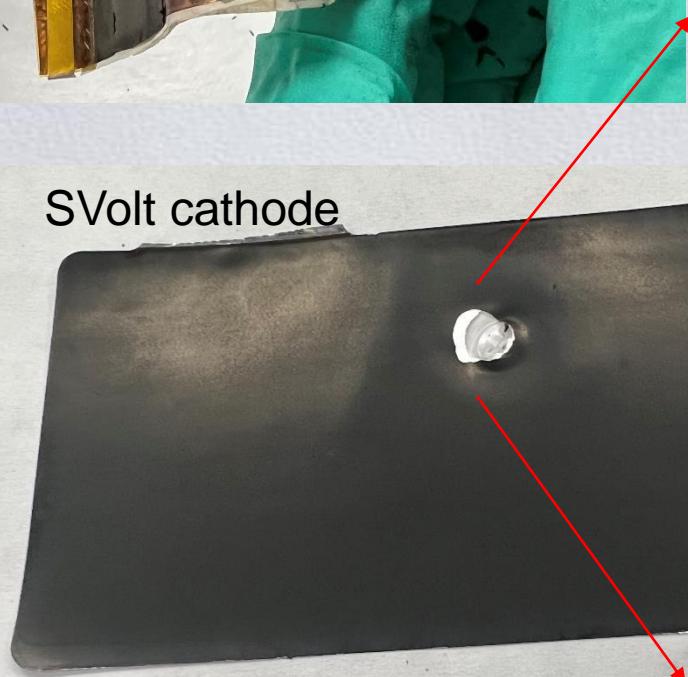
DPA Reveals Thermal Effect in PCC Response



Anode & Cathode PCC



Anode & Cathode PCC



- Difficult unwinding due to melting of polyester CC and polyolefin separator ending glued together at nail interface
- Nail hole reveals thermally stressed PCC

Forward Work

- Reduce high speed X-ray videographic data of all runs
 - Insights from higher magnification field of view (FOV)
- Examination of nail surviving cells with micro fine resolution CT
 - Focus on PCCs at nail interfaces
 - Explore cross sectioning cells for further insight into the nail interface
- Improve FTRC for ISCD cells
 - Redesign cell chamber with lower mass and heater localized near ISC device on cell can
 - Shut-off heater at OCV dips, discharge the cells, and CT/DPA the cells to confirm activation of the ISC device
- Order higher energy Li-ion cells with and without PCCs

Summary of our 2022 Effort

Feb 2022

Soteria polyester PCC much more reliable in tolerating nail penetration in 37 out of 38 Li-ion cells tested in 2022

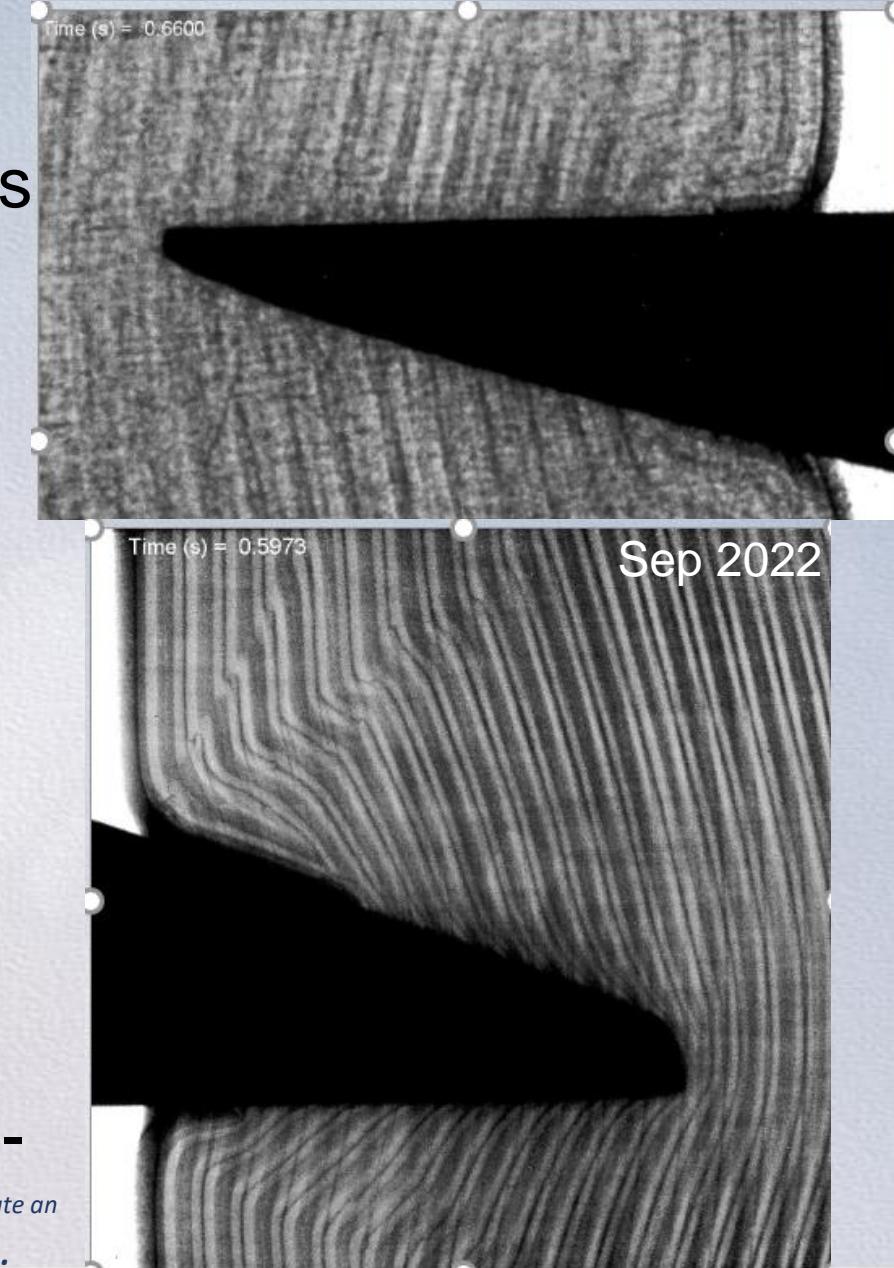
- 2.1Ah Coulometric 18650s (18 for 18)
 - And 3 for 5 for Nomex PPCs
- 2.75Ah BAK 18650s (6 for 6)
- 4.5Ah BAK 21700s (5 for 6)
- 10Ah SVolt Pouch Cells (8 for 8)

Evidence for mechanism grows

- Vaporization of the polyester collector at nail interface more clearly shown in radiographs

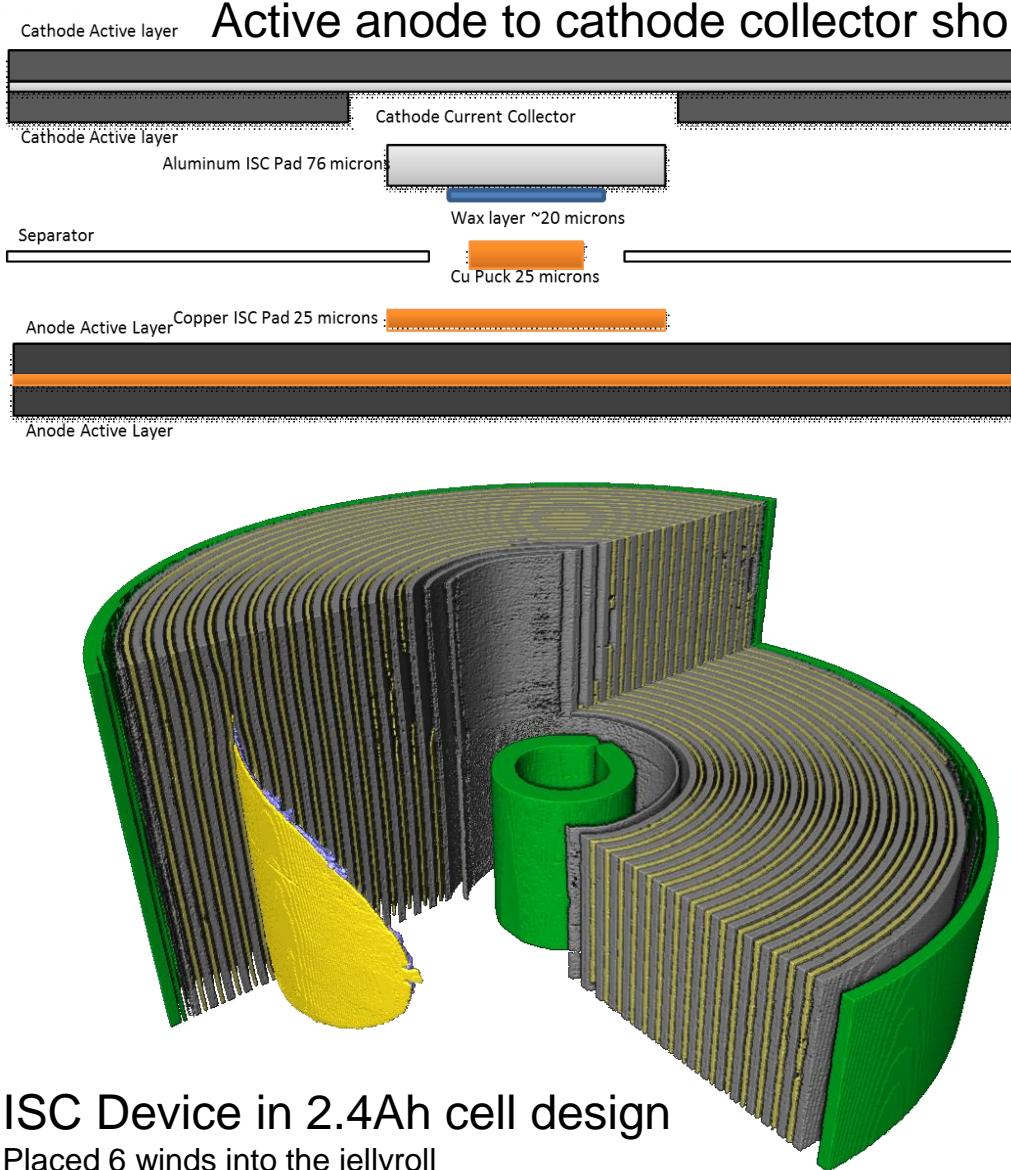
Very promising technology but

- Tab-to-collector welding challenges remain
- Will they work in highest energy (≥ 275 Wh/kg) Li-ion cells?

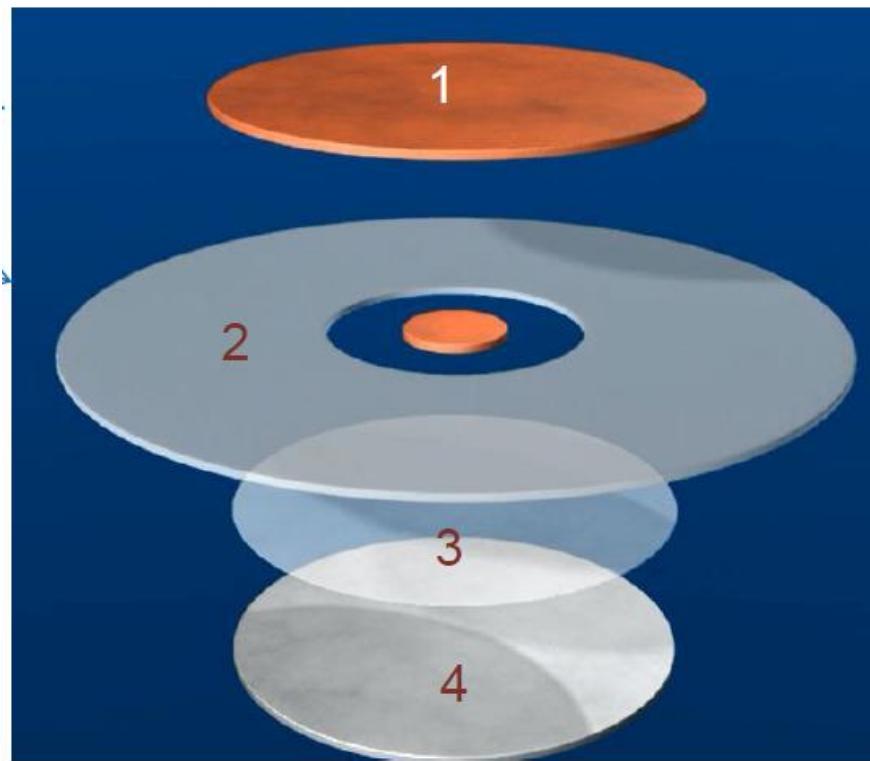


Back Up

NREL/NASA Cell Internal Short Circuit Device



Exclusive Licensee, March 2018



Graphic credits: NREL

Top to Bottom:

1. Copper Pad
2. Battery Separator with Copper Puck
3. Wax – Phase Change Material
4. Aluminum Pad

2010 Inventors:

- Matthew Keyser, Dirk Long, and Ahmad Pesaran at NREL
- Eric Darcy at NASA

US Patent # 9,142,829
issued in 2015

Thin (10-20 μm) wax layer is spin coated on Al foil pad

Wax formulation used melts $\sim 57^\circ\text{C}$

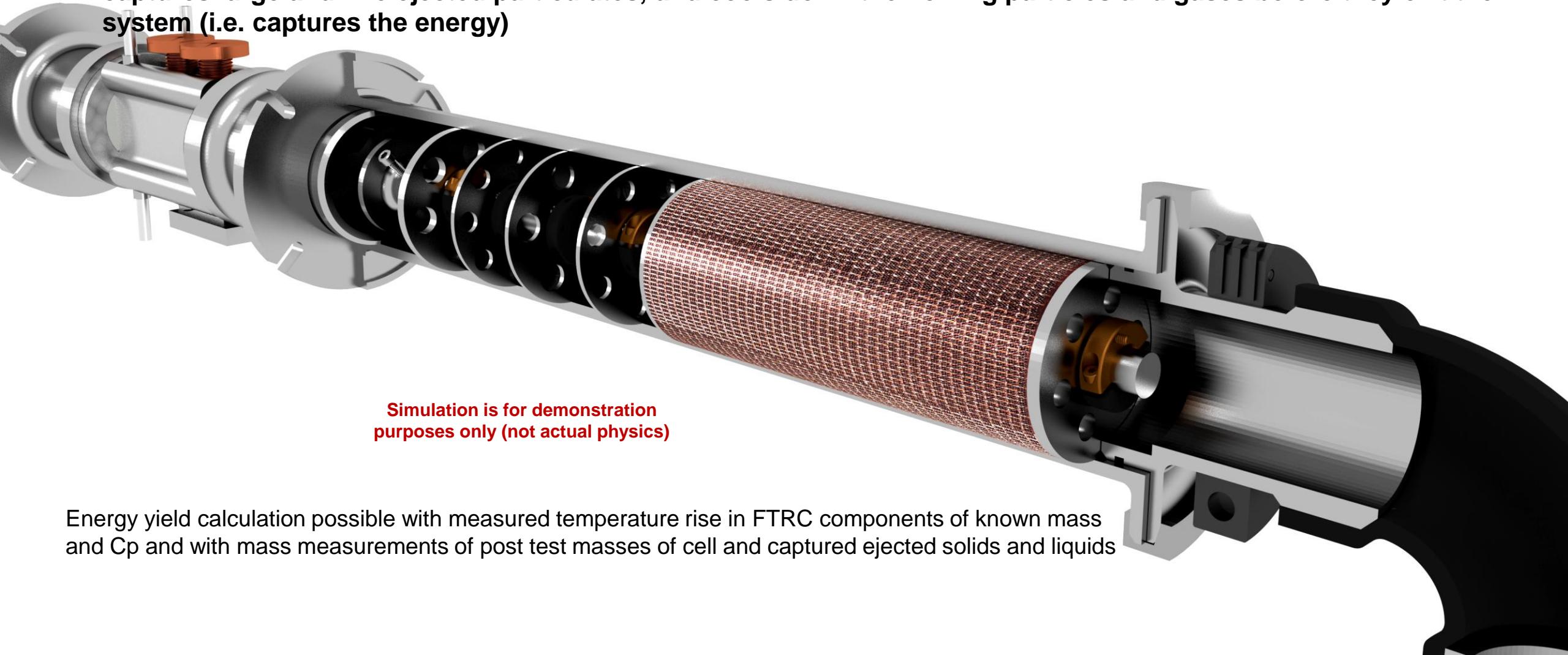
Runner-up NASA Invention of 2017

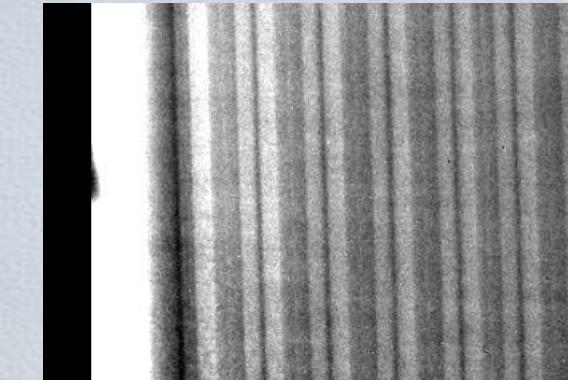


2016 Award Winner

FRACTIONAL THERMAL RUNAWAY CALORIMETRY (FTRC)

- The internal baffles and copper mesh are used to create a tortuous path that effectively reduces flow velocity, captures large and fine ejected particulates, and cools down the flowing particles and gases before they exit the system (i.e. captures the energy)



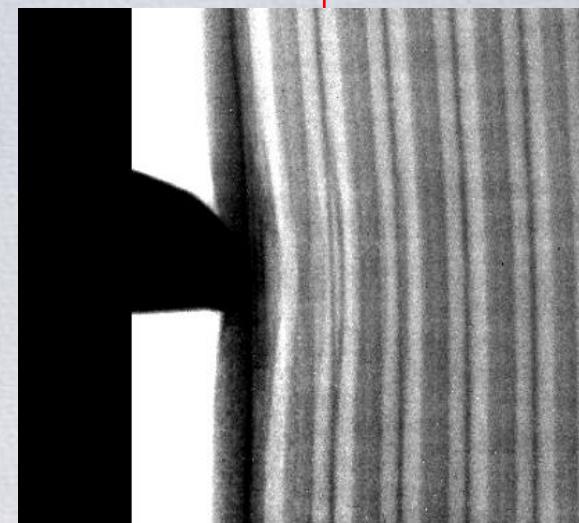


Bright electrode is anode with dense materials showing as dark

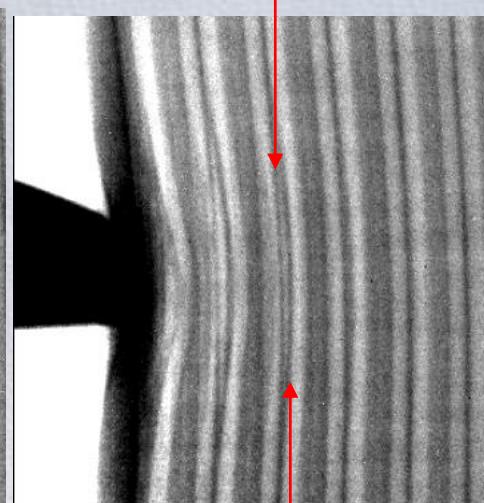
Each snapshot is successive (~300 fps or 3.3 ms increments)



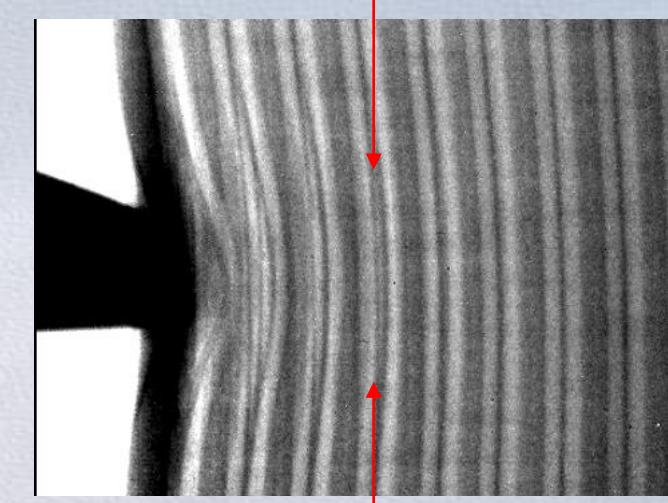
1st CC local swelling



2nd CC local swelling

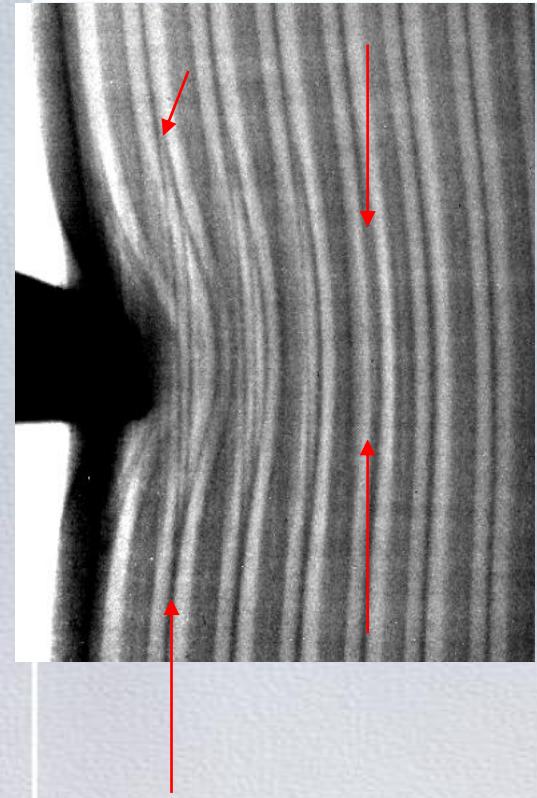


3rd CC local swelling

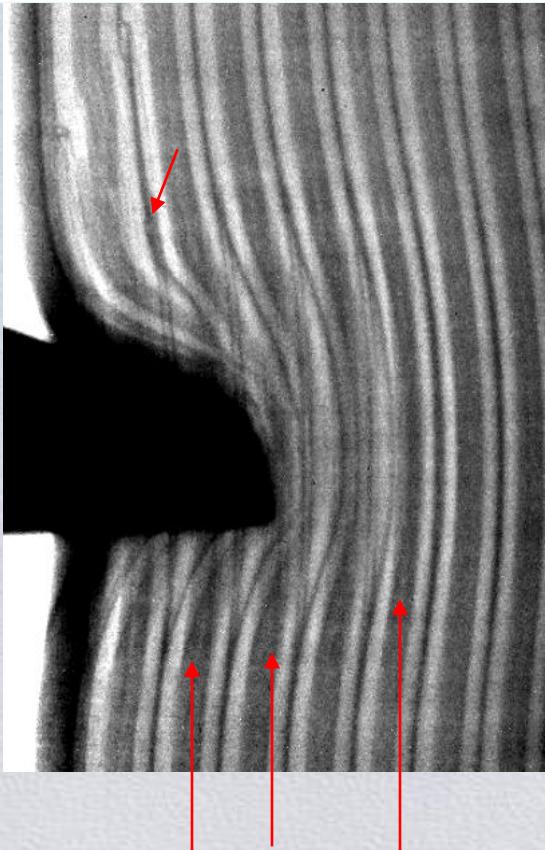


As the nail compresses the can wall, the outer wind is locally compressed and the anode CC bulges with a bright inner layer surrounded by CC or gap. In the next frames, the bulging increases as more deformation occurs in that outer wind. The pattern repeats for the 2nd and successive winds.

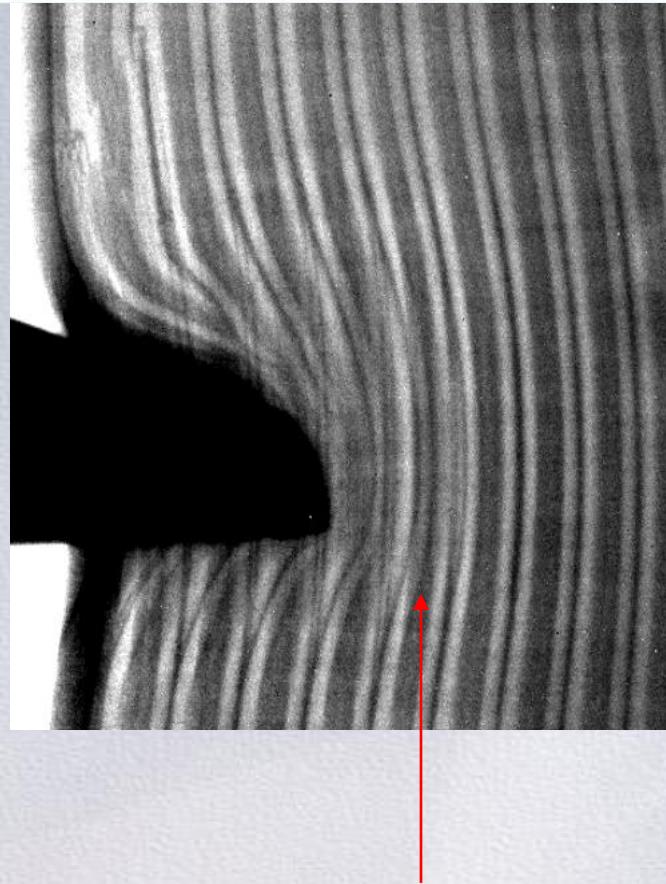
We may be seeing a mechanical phenomena at these early stages as it takes more time for a thermal effects to develop.



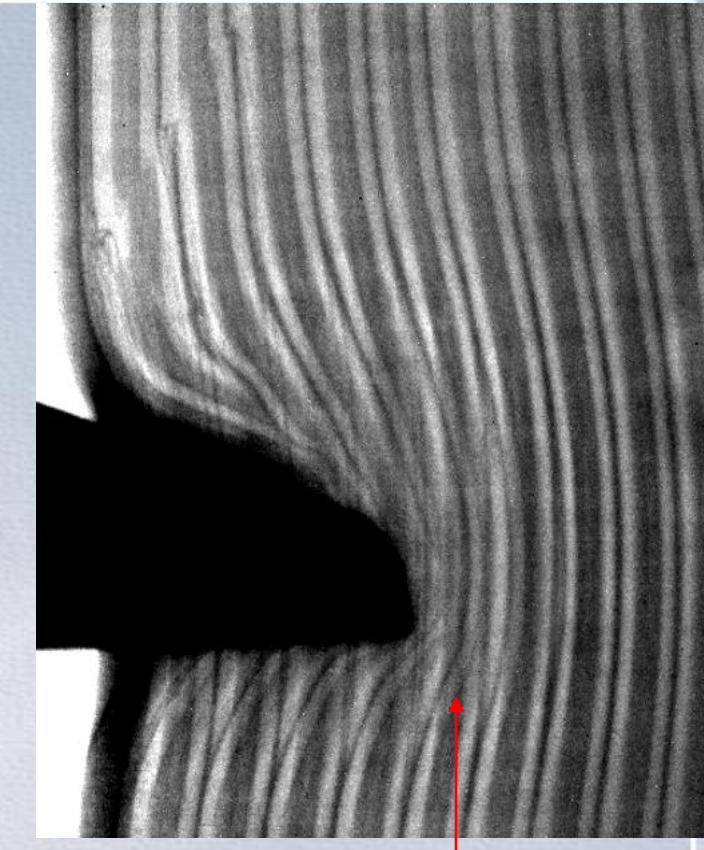
As the 2nd wind fluidizes next to nail, gap opens at PCC



Nail pushes wedge of NMC down into PPC gap

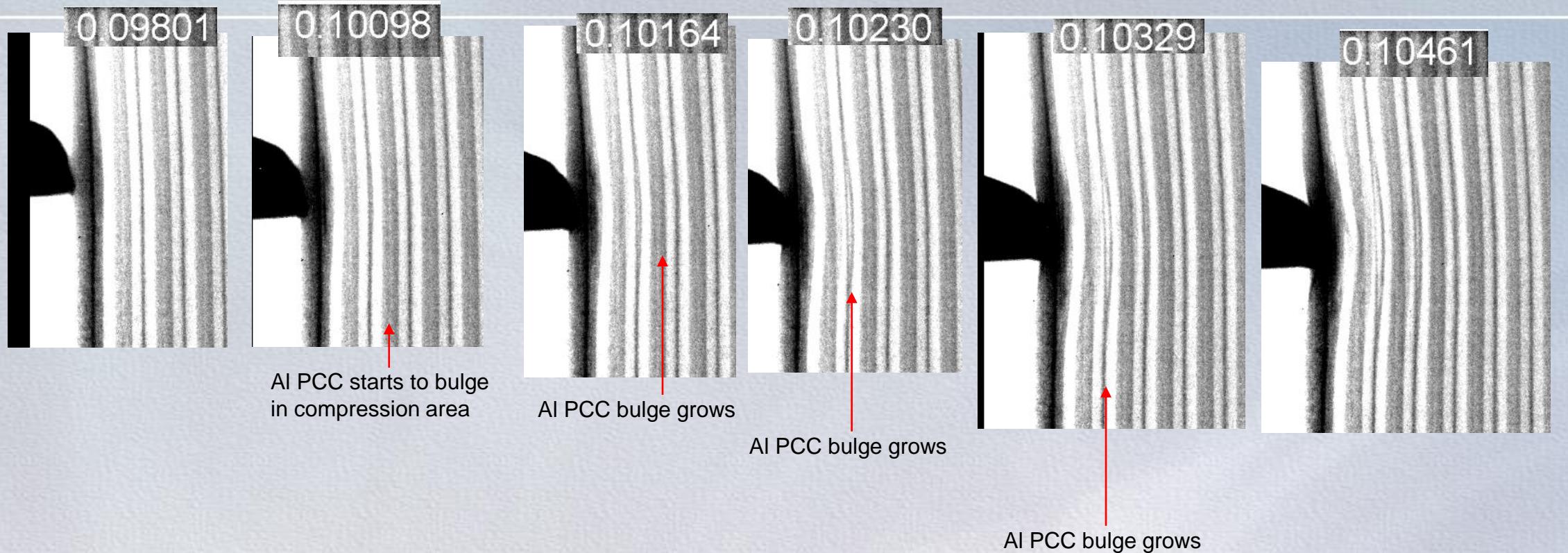


NMC loses density due to shorting



NMC in front of nail turns gray as layers are compressed

NMC at nail interface turns grayer



PCC Against ISC Device (Heat trigger)

- 2.1Ah Coulometric 18650 cells
 - Metalized polyester PCC (6)
 - Cathode only all 3 went into TR
 - Anode and cathode 1 of 3 survived
 - Metalized Nomex PCC (2)
 - Cathode only went into TR
 - Anode and cathode PCC went into TR
 - Control cells all 4 went into TR
- 3.6Ah Amprius Pouch Cells
 - Soteria metalized polyester (3)
 - PCC on cathode only
 - 100% Si anode with Ti collector
 - Results (one of each)
 - 100% SoC went into TR
 - 70% SoC went into TR
 - 30% SoC experienced no TR
 - Control Amprius cells (3)
 - Al collector on cathode & Si anode
 - Results (one of each)
 - 100% SoC went into TR
 - 70% SoC went into TR
 - 30% SoC went into TR

Note that heat applied to cell chamber overwhelmed the cell thermally and drove TR even after PCC appeared to isolate the ISC device.

New cell chamber designed for triggering ISC devices with minimal heat is under development